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## **BASE HYDROLYSIS PROCESS FOR THE DESTRUCTION OF ENERGETIC MATERIALS**

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January 2002



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TANK AUTOMOTIVE AND  
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Commissioning of the energetics hydrolysis system was successfully accomplished at Holston Army Ammunition Plant on 14 December 2000 with the first trial run with Composition B explosive. The test and evaluation program was completed in April 2001.

The results of the testing indicate that the base hydrolysis process for energetics is robust, reliable, and flexible. The process will easily achieve destruction rate efficiency (DRE) ranging from 99.75% to 100% versus a goal of 99.999%. Where the 99.999% goal was not achieved (the sampling and analysis procedure may have contributed to the lower than desired DRE), the hydrolysate could be safely processed by the final treatment step. The concerns identified by the NRC were satisfactorily addressed; i.e., the by-products of full-scale processing of energetics are relatively benign.

The formation of Picric Acid as a by-product of energetics hydrolysis is not considered a problem. Picric Acid was only detected at very low levels in the mid-run analyses for Tetrytol and was detected at even lower levels in the end of run analyses. This conclusion is supported by the bench-scale work performed by Los Alamos National Laboratory that showed no Picric Acid present in the hydrolysate.

Processing energetic mixtures presented no problems and can be safely performed with the process. Los Alamos National Laboratory performed substantial bench-scale testing to support this effort and expand the database for the hydrolysis of energetics.

Two processing concerns were identified during the program: the handling of the rayon bags containing the M1 propellant charge, and the handling of the cotton threads used to bundle the M8 sheet propellant. Both warrant further study.

The full-scale system performed satisfactorily from an equipment standpoint. The only problem encountered was the feeding of the dry energetics using a loss-in-weight feeder. There were several improvements identified that were not implemented because of the severe schedule; and for the most part, these improvements were directed at improving data collection and not to address processing deficiencies.

The energetic hydrolysis system was successfully demonstrated on a pilot-scale and is recommended for inclusion in the design package for the Pueblo and Blue Grass Chemical Agent Disposal Facilities.



## **FINAL REPORT**

**December 2001**

# **Base Hydrolysis Process for the Destruction of Energetic Materials**

Prepared for: Program Manager, Assembled Chemical Weapons Assessment  
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## **Executive Summary**

The Program Manager, Assembled Chemical Weapons Assessment (PM ACWA) was formed by Public Law 104-208, Sec. 8065 to study alternatives to the baseline incineration process for the demilitarization of assembled chemical weapons, and that at least two alternatives to the baseline incineration process be identified and demonstrated. The information generated under the PM ACWA program will be used to support a technology decision for the Pueblo, Colorado and Blue Grass, Kentucky Chemical Agent Disposal Facilities.

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Tank-Automotive and Armaments Command - Armament Research, Development and Engineering Center was tasked by PM ACWA to execute an Engineering Scale Test of the base hydrolysis process. The objective of this program was to: determine optimum operating parameters to support scale-up of the hydrolysis process, define a hydrolysis process that is safe and environmentally compliant; and address issues regarding full-scale hydrolysis of energetics identified by the National Research Council (NRC) reviewing technical progress on the ACWA program.

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The formation of Picric Acid as a by-product of energetics hydrolysis is not considered a problem. Picric Acid was only detected at very low levels in the mid-run analyses for Tetrytol and was detected at even lower levels in the end of run analyses. This conclusion is supported by the bench-scale work performed by LANL that showed no Picric Acid present in the hydrolysate.

Processing energetic mixtures presented no problems and can be safely performed with the process. Los Alamos National Laboratory performed substantial bench-scale testing to support this effort and expand the database for the hydrolysis of energetics.

Two processing concerns were identified during the program: the handling of the rayon bags containing the M1 propellant charge, and the handling of the cotton threads used to bundle the M8 sheet propellant. Both warrant further study.

The full-scale system performed satisfactorily from an equipment standpoint. The only problem encountered was the feeding of the dry energetics using a loss-in-weight feeder. There were several improvements identified that were not implemented because of the severe schedule; and for the most part, these improvements were directed at improving data collection and not to address processing deficiencies.

The energetic hydrolysis system was successfully demonstrated on a pilot-scale and is recommended for inclusion in the design package for the Pueblo and Blue Grass Chemical Agent Disposal Facilities.





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## **1.0 BACKGROUND**

PM ACWA was formed as a result of Public Law 104-208, Sec. 8065 that mandates a study of alternatives to the baseline incineration process for the demilitarization of assembled chemical weapons. At least two technologies must be demonstrated that will address all aspects of demilitarization of all components of each of the chemical weapons in the stockpile. The chemical weapon storage sites supported by the ACWA program are located at Pueblo Army Ammunition Depot (AAD), Pueblo, Colorado and Blue Grass AAD, Lexington, Kentucky.

### **1.1 Candidate Technologies.**

PM ACWA identified 6 candidate technologies that warranted further evaluation. Three of the technologies were evaluated on a bench-scale in FY 99:

- Bio-treatment (combined hydrolysates)
- Plasma arc
- Super critical water oxidation (SCWO)

Upon completion of the evaluation of these candidate technologies, the stakeholders ((public interests groups including Green Peace, the Sierra Club, local and state government representatives, subject matter experts, etc.) successfully petitioned Congress to provide additional funding to evaluate the remaining three candidate technologies: (see Appendix A for acronyms and abbreviations.)

- Solvated electron technology (SET)
- Gas phase chemical reduction (GPCR)
- SILVER II technology

These evaluations were conducted in the FY 00 and FY 01 time frame. The PM decided to conduct additional work to characterization and optimize the base hydrolysis process for energetic materials based on comments and recommendations received from the National Research Council (NRC) (Appendix B reviews the NRC concerns) regarding the base hydrolysis process for energetics (the NRC is independently reviewing the results of the ACWA program). Base hydrolysis is an intermediate process step used to de-energize the energetic materials (explosives and propellants) recovered from the chemical munitions during the disassembly operation. The hydrolysate produced during the hydrolysis of the energetics is sent to a final destruction process.

### **1.2 Energetics Hydrolysis System.**

TACOM-ARDEC was tasked by PM ACWA to conduct engineering scale testing (EST) with a pilot-scale hydrolysis system capable of processing all energetics (explosives and propellants) found in the chemical weapons stockpiled at the Pueblo and Blue Grass AADs. The system was to be full-scale capable of processing up to 500-pounds per hour of energetics.

#### **1.2.1 EST Energetics Hydrolysis System Program Team:**

The government team was comprised of government personnel from TACOM-ARDEC (technical managers of the program), Holston Army Ammunition Plant (AAP) (installation site for the energetics hydrolysis system), Radford AAP (manufacturing site for M28 surrogate propellant), and the Naval Surface Weapons Center. The contractors and OGAs supporting the EST effort included Royal Ordnance North America (operating contractor of Holston AAP), Alliant Techsystems (operating contractor for Radford AAP), IPS, Inc., Pfudler, Inc., Pantex, Inc., and Los Alamos National Laboratory (LANL). Sample collection was overseen by A.D. Little, Inc. with TRC Inc. providing and manning the off-gas sampling system that was interfaced to the reactor.

## 2.0 PROGRAM OBJECTIVE

The objective of the TACOM-ARDEC Energetics Hydrolysis System EST program is to:

- Address concerns identified by the National Research Council (NRC) and processing issues that surfaced at Radford AAP and PANTEX, Inc. during the manufacturing of the various hydrolysates used to support the previous demonstration testing
- Determine the optimum process operating parameters to support scale-up of the hydrolysis process and the definitization of the Engineering Design Package (EDP) for the pilot phase for the Pueblo Chemical Agent Disposal Facility scheduled in August 2001 and for the Blue Grass Chemical Agent Disposal Facility scheduled in August 2002.
- Define a hydrolysis process that is safe and environmentally compliant, and that will efficiently produce hydrolysates of energetic materials recovered from the various chemical munitions during the disassembly process.
- Produce hydrolysates that will be ready for post-treatment processing using such technologies as SCWO, bioreactor, etc.

The hydrolysis process defined under this program will provide the flexibility to process the full range of material conditions that may be encountered with the recovered energetics, and to produce hydrolysates that conform to the material stream requirements dictated by final post treatment process.

### 2.1 Energetics Hydrolysis Pilot Plant Layout.

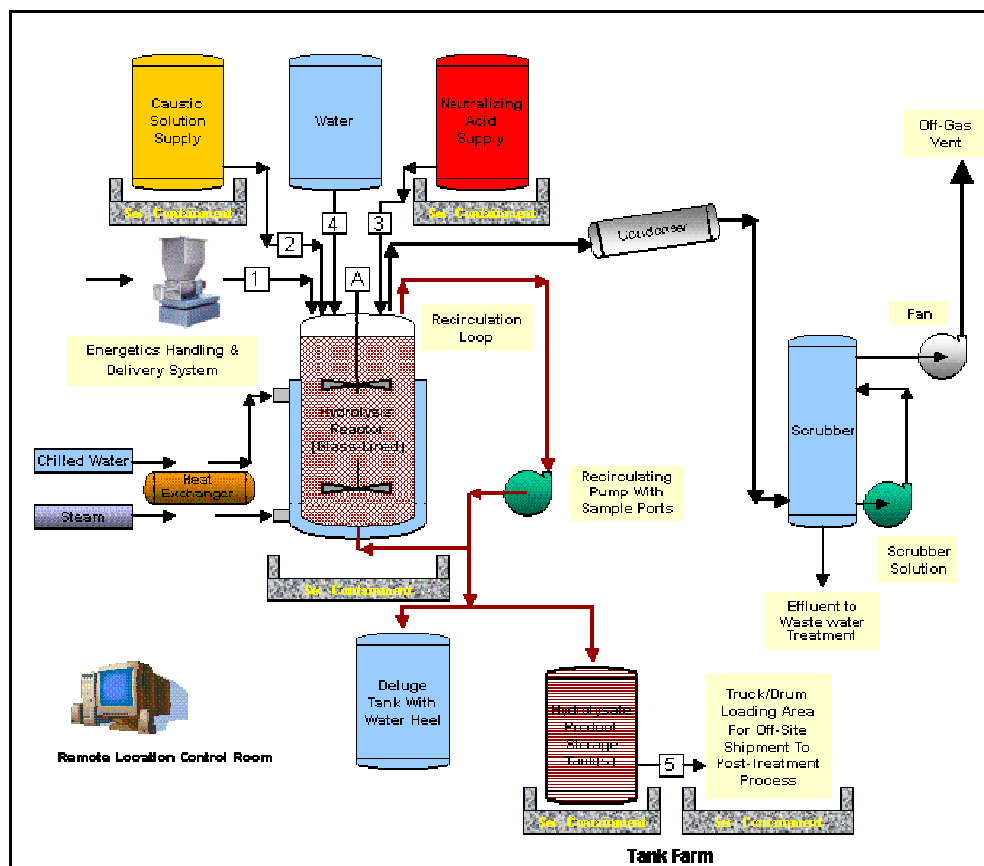


Figure 2-1. Process Schematic of the Energetic Hydrolysis Process



## **2.2 Bench Scale Testing in Response to NRC Concerns.**

NSWC and LANL were tasked to perform bench scale testing to address the NRC concerns. The thrust of this effort is:

- Evaluate temperature-time-pressure relationships of the energetic materials in aqueous alkaline solutions of sodium hydroxide
- Quantify the heat of reactions
- Determine the solubility of energetics in specific alkaline solutions,
- Assess the simultaneous processing of different types of energetics, and
- Determine the particle size reduction of energetics that must be achieved for proper post-treatment operation

LANL has issued two reports (refs. 1 and 2) detailing the bench-scale efforts.

The work performed by NSWC is not being reported. The results of the accelerated colorimeter work were inconsistent, most likely due to the reactivity of the sample before insertion into the ARC.

## **2.3 M28 Surrogate Propellant and Hydrolysate.**

M28 surrogate propellant was manufactured at Radford AAP to support the technology demonstrations, as well as the testing of the hydrolysis at Holston AAP. A leaded (lead stearate per the formulation requirements) and unleaded version of the propellant was produced by Alliant Techsystems. In two cases, the propellant was hydrolyzed at Radford AAP and shipped to the technology providers (the hydrolysis system was not available at the time of these efforts) using a simple stirred heated open tank. During the second hydrolysis run, an incident occurred during the hydrolysis reaction that resulting in an over-pressure and rupturing of the piping loop supporting the hydrolysis tank. The damage to the equipment was minor. The description of the M28 manufacturing process and the incident report are included in references 3 and 4.

### 3.0 SYSTEM AND HARDWARE DESCRIPTION / OPERATIONS

The energetics hydrolysis system is comprised of the following major subsystems.

#### 3.1 Energetic Feed System.

An Acrison, Inc. Model 402-1015Z weight-loss feeder was used to feed dry energetics to the hydrolysis reactor. The unit had a 500-pound working capacity with a feed rate range of 20- to 3000-pounds per hour. The unit contained a conditioning auger in the feed bin to prevent material compaction or bridging. All parts that contacted energetics were fabricated of 304 series stainless steel. The unit was fully gasketed for water wash-down. The weigh-feeder was located on the 3<sup>rd</sup> floor in Building G-10, mounted onto a work platform. The energetics was manually charged into the hopper before the start of the test run. The energetics discharged from the metering auger fell through a 6-inch diameter stainless steel chute into the reactor (gravity feed).



Figure 3-1. Acrison Loss-in-Weight Feeder

The unit was capable of continuous or batch weighing. Located on the platform above the feed hopper was a 1-inch by 1-inch screen (stainless steel) that served as a final screening of the material before entering the bin.

The weight-feeder was isolated from the reactor using upper and lower slide-gate valves (Figure 3-2). The slide valves operated in tandem, sequenced to ensure that energetic material was not captured within the down-comer chute. All energetics materials with the exception of the M8 sheet propellant were processed using this system configuration.

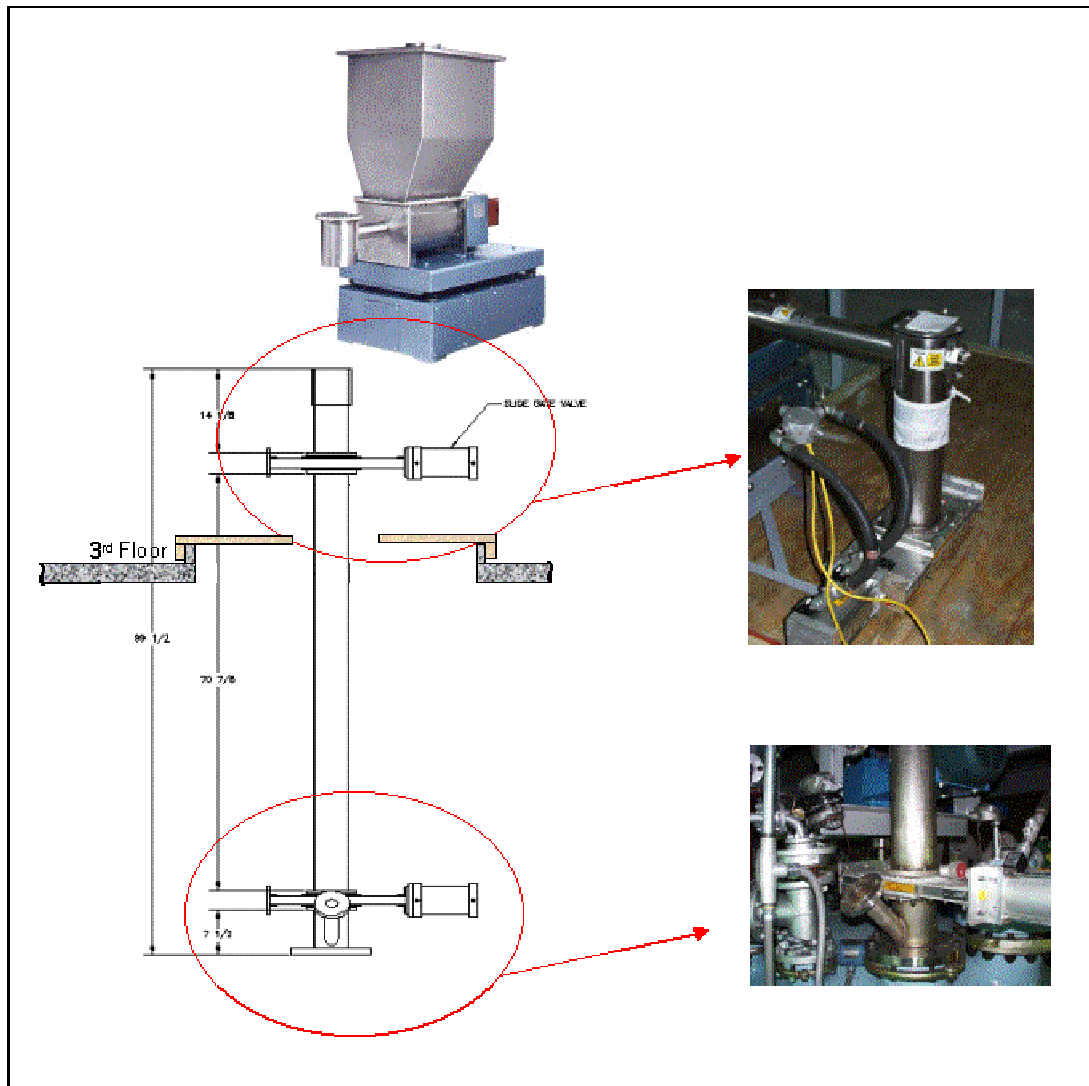


Figure 3-2. Slide Valve and Feed Chute Assemblies

The M8 sheet propellant was manually fed to the reactor, by-passing the weigh-feeder, because of its configuration. The interface between the weigh-feeder discharge and the down-comer chute was modified as shown in Figure 3-3. An operator manually fed the M8 sheet propellant into the hopper at a rate approximating the required pounds per hour feed rate selected for the test.

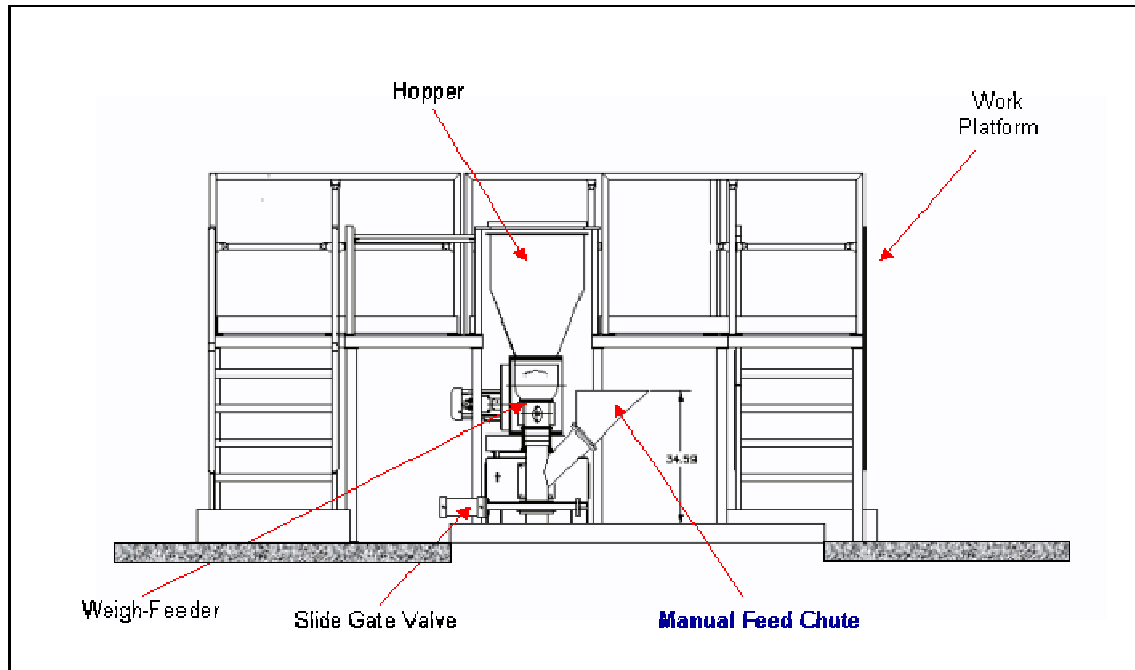


Figure 3-3. Manual Feed Chute Used with M8 Sheet Propellant

### 3.2 Tank Farm.

Sodium hydroxide and sulfuric acid and/or nitric acid are stored in the tank farm adjacent to Building G-10. The tank farm also served as a storage area for the hydrolysates produced during testing.



Figure 3-4. Tank Farm Servicing Building G-10

### 3.3 Hydrolysis Reactor.

Pfaudler, Inc. fabricated the reactor vessel complete with structural supports, work platform and walkway. The vessel is a Pfaudler RS-78-2000-125-100 glass lined carbon steel RS-Series reactor; 2000-gallon capacity; 78-inch diameter by 84-inch straight side; conventional single chamber carbon steel jacket; ASME design and stamp for 125 psig/FV at -20 to 450°F internal and 100 psig/FV at -20 to 450°F jacket (90 psig with full internal vacuum); with 9115 blue Glasteel® surface. The cover contains two, 10-inch flanged ports; one 8-inch flanged ports; one, 6-inch flanged ports; and five, 4-inch flanged ports. The heating capability of the reactor is 1,500,000 BTU/hr; the cooling capability is 500,000 BTU/hr.

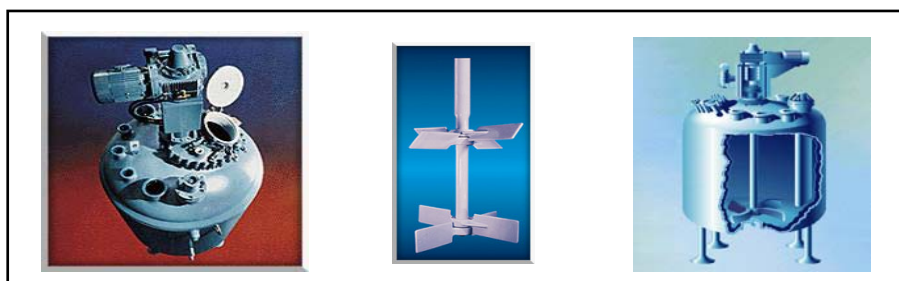


Figure 3-5. Pfaudler Hydrolysis Reactor (Typical Representation)

The system as delivered partially assembled from Pfaudler, Inc. and included following design features and ancillary systems:

- Interior surfaces configured to minimize accumulation of precipitates
- Glasteel® cover-mounted baffles to promote mixing/distribution of energetics
- Fin-type Glasteel® baffle with tantalum encased RTD
- Tachometer for monitoring and controlling agitator speed
- Great Lakes Model 692P Two-Wire pH Transmitter
- Krohne Level-Radar Sensor BM 70 A
- Chemineer Model 2HTD-10 Turbine Agitator, Hastelloy C-276, Turbofoil upper and lower pitched-blade impellers (10 HP)
- Toshiba variable frequency controller (VFC) for use with Chemineer Agitator System
- Rosemount Series 8700 Magnetic Flowmeter Systems for caustic, acid and water
- Heat Exchanger – Reactor Jacket, Kam Thermal Equipment Ltd. (143 ft<sup>2</sup>), 304L stainless steel tube side, carbon steel shell
- Heat Exchanger – Condenser (43 ft<sup>2</sup>) with Hastelloy C-276 tube side, carbon steel shell
- Dual discharge port valves
- Process piping 316L stainless steel, Hastelloy C-22, Teflon lined
- Feed ports and analytic sampling ports for solids and liquids
- HYL80 Toroidal Explosion-proof Process Light
- Manway cover, 24-inch diameter (spring assist with fused sight glass) for maintenance
- Auxiliary water seal assembly per RONA design requirements
- Reactor support frame and work platform with walkway

To avoid building pressure within the reactor from off-gassing released during the base hydrolysis reaction, outside air was continuously be drawn through the vessel carrying the off-gassing from the reactor to a condenser and then on to a scrubber/stripper/absorber system before venting to atmosphere to ensure that no toxic chemicals are released to atmosphere. The off gassing was analyzed for the presence of NO<sub>x</sub>, CO<sub>2</sub>, CO, TOC, and others using online analyzers (see paragraph 3.9 below).

The design of the agitator was determined by Pfaudler, Inc. based on the volume of the reactor vessel and the requirement to ensure that the solution is maintained homogenous throughout hydrolysis reaction. The detailed specifications and drawings for the Pfaudler reactor including ancillary equipment are provided in reference 5.



Figure 3-6. Turbofoil Pitched-Blade Agitator

A pH control system was installed on the reactor to maintain a required/specified pH for post-treatment operations. The unit was located in the recycle line. However, as expected, at the higher caustic levels, pH greater than 9, the sensor would go off-scale and proved useless with regard to being used as a process control and monitoring device. Therefore, the installation of the pH meter was more experimental in nature (to assess hardware performance as a potential means of controlling the pH of the hydrolysate solution and the neutralization process) as opposed to being needed for process control.

### 3.4 Liquid Sampling System.

A liquid sampling system, Intersystems Sampling System, Model LF, was flange-mounted on the recirculation line. The sampling probe is 1-inch in diameter fabricated of 316 series stainless steel with TFE seals. Each sample is approximately 10-ml. The sampling rate is programmable from 0.01 to 999 hours. The unit is supported by a 16-station carousel mounted in an enclosure capable of being chilled using ice or dry ice. All controls are explosion-proof. The pressure rating of the sampler is 150 psig and the temperature rating is 500°F.

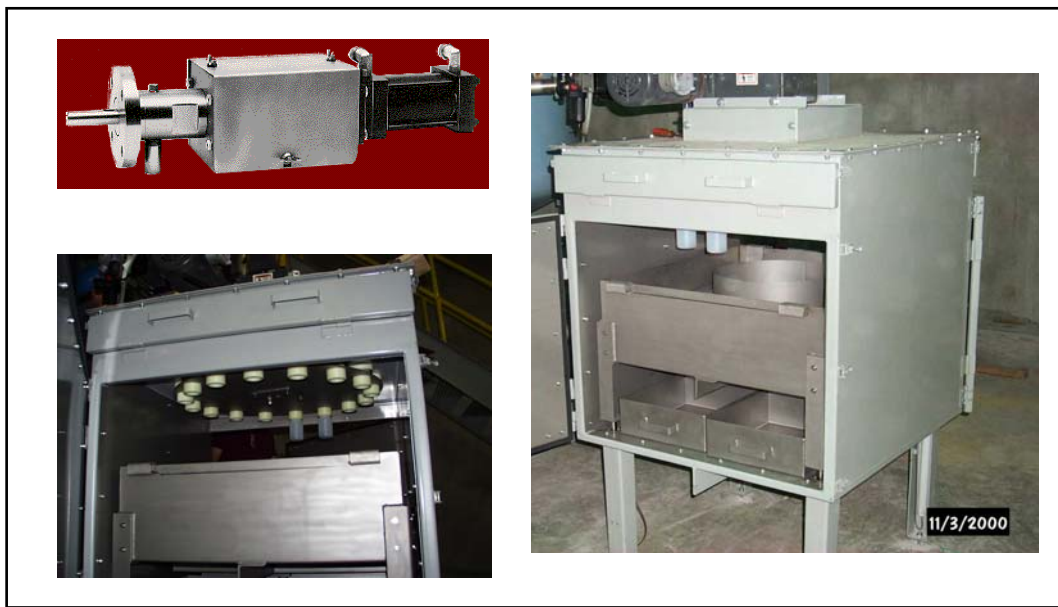


Figure 3-7. Liquid Sampling System

There are sixteen index positions on the carousel; each position has a 250-ml HDPE sample bottle into which the sample is drained.

#### 3.4.1 Typical Sampling Procedure:

The following procedures was developed based discussions with A.D. Little, Inc. and LANL:

Sample Bottle Preparation: In an attempt to maintain the hydrolysate sample at the conditions at which it was taken, the collected samples were quickly quenched in sulfuric acid and chilled to  $-4^{\circ}\text{C}$  in ice. To accomplish this, an acid heel is placed in each sample bottle before the bottle is mounted on the carousel, typically 30 ml of sulfuric acid (6 normal). The cabinet is packed with ice to maintain the  $-4^{\circ}\text{C}$  temperature.

Sampling: A single sample was comprised of SIX sample aliquots that were injected into the sample bottle on the carousel (the sampler was programmed to cycle the injector six times). The total volume of these six sample aliquots would be approximately 42 milliliters (i.e., ~7 ml per sample aliquot).

Flush: After the six aliquots were injected into the sample bottle, the sampler / tubing was flushed with 100 ml of distilled / deionized water to "clean" the system into the sample bottle. The water was fed into the sample line immediately below the sampling valve to ensure that the water would "flush" across all of the areas that had been "wetted" by the hydrolysate sample. After the flush, the sample carousel would be indexed to the next sample position and the sampling sequence repeated.

The total volume in the sample bottle as it was taken from the sampler unit was about 172 ml consisting of 100 ml flush water, 30 ml of 6N sulfuric acid heel, and approximately 42 ml hydrolysate sampled from the reactor. Typically, sixteen samples would be collected during an experimental run. The samples are packaged per A. D. Little, Inc. specification and sent to an independent laboratory through A. D. Little, Inc. for analysis and reporting of the results, as required by the test protocols establish for the ACWA program.

#### 3.4.2 Hardware Modifications:

Two modifications were made to the liquid sampling system to improve performance: A purge line was installed into the system immediately below the sampling valve in the recirculation line so that the sampling mechanism and line could be flush with distilled / deionized water to clean the system and prevent / minimize "carry-over" between samples. A vessel of distilled / deionized water (20 liter Nalgene bottle) was stored on the third floor of Building G-10. By remotely opening a needle valve for a specified time period (typically 15 seconds, which correlated to about 100 ml of water), the water would be gravity fed into the system as the purge. A small hole (1/16-inch) was drilled in all of the plastic holders / lids (16 in total on the carousel) into which the 250-ml sample bottles were threaded and suspended. This hole provided venting for the bottles during the introduction of liquid hydrolysate or flush, which prevented the sample bottles from pressurizing.

#### 3.5 End of Run Liquid Sample.

At the end of each experimental run, a bulk sample would be taken using a series of valves, which could be opened in the recirculation line (while the hydrolysate was being pumped through the line). In practice, approximately 4 liters of the hydrolysate would be collected in a 4-liter volume HDPE jug to "flush" the line / valve and then discarded. Immediately after this flush, hydrolysate would be collected in additional jug(s) as the "end-of-run" sample. The volume of this "end-of-run" sample would be either 4 liters or 8 liters as specified by A. D. Little, Inc. personnel.



### 3.6 Control System.

The energetics hydrolysis process in Bldg. G-10 was fully automated and remotely controlled from the Central Control Building, Building 155 via a fiber optic link to the process area. The process displays were generated using PCS7-WinCC software.

Figure 3-7 shows the operator in the Control Room interfaced to the process floor along with process flow diagram displays of the controlled and operating process parameters

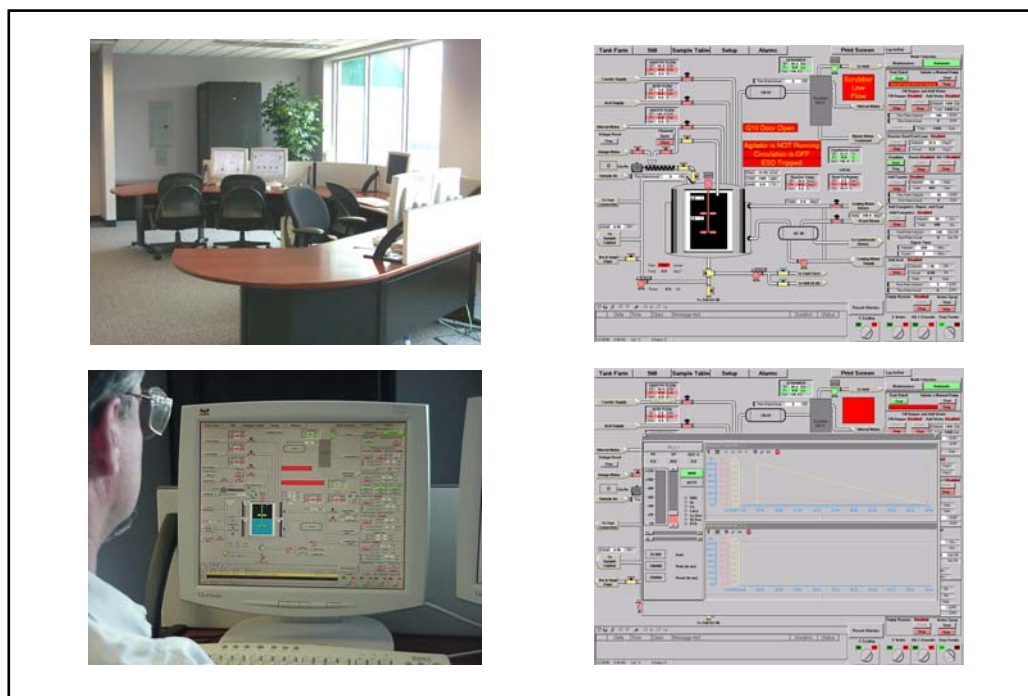


Figure 3-8. Central Control Room, Process Displays

The PCS7-WinCC software was used to plot key process operating and control parameters for each run of the runs reviewed in paragraph 6 (unless otherwise noted). An example of this chart is shown in Figure 3-8 (the operating data for commissioning Run 4, Composition B explosive) where:

- **Energetic Feed Rate:** This will normally be represented as a step function over a four-hour period corresponding to the feed rates cited above.
- **Hydrolysate Temperature:** This represents the temperature of the hydrolysate in the reactor during the process.
- **Reactor Jacket Temperature:** This is the temperature of the cooling/heating medium within the jacket of the reactor.
- **Reactor Outlet Flow:** This is the airflow through the reactor headspace to the scrubber. The airflow was maintained at ~40 scfm throughout the tests
- **Reactor Air Sweep:** This is the amount of air flowing into the reactor headspace during the processing of the energetics.

The data logger ran continuous both while the process was underway and during non-processing periods. In addition to the data presented on the charts, the agitator speed, valves settings,

energy consumption of pumps, level flow rates, etc. were logged continuously and could be plotted “real time” at the discretion of the operator to evaluate trends and/or create a hard copy of specific test data..

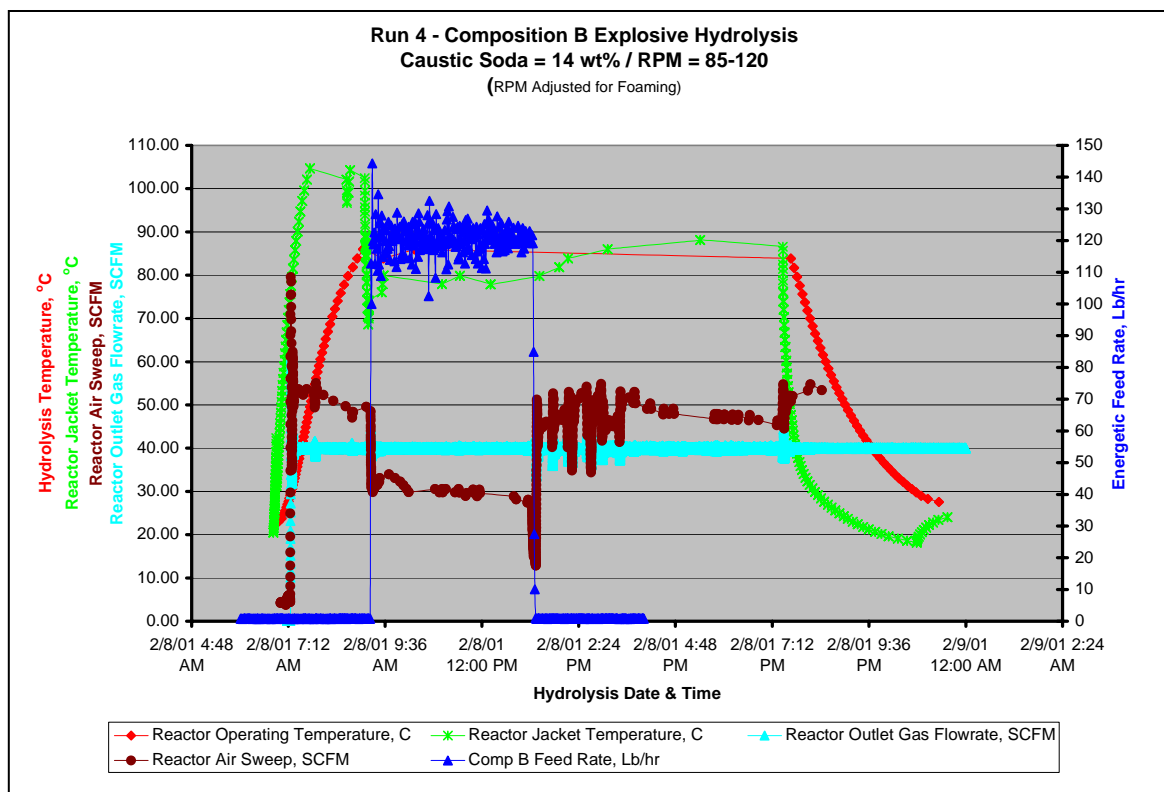


Figure 3-9. Process Operating and Control Parameters

The plot presents the explosive addition at a rate of ~125 lbs/hr over a four hour period, the hydrolysate temperature versus the jacket temperature, and the sweep air and make-up air flowing across the reactor head space. The agitator speed was varied during the run between 85-to-120 rpm to control the foaming that was encountered during process commissioning. Data can also be recovered for the rpm, current draw on the recirculation pump, etc. These processing parameters may be plotted against time. However, to keep the chart simple, only the five process variables presented above were plotted for each of the test runs.

### 3.7 Process Description.

The alkaline solution will be introduced into the reactor from the tank farm adjacent to Building G-10, the pH adjusted through introducing process water to the caustic solution, and heated to a desired temperature by circulation steam or heating fluid through the reactor jacket. While the caustic solution is being prepared, the energetic material to be process will be charged into the weigh-feeder hopper located on the 3<sup>rd</sup> floor. When the caustic solution reaches the required temperature, the energetic materials are added into the reactor using the weigh-feeder system on the 3<sup>rd</sup> floor.

During the addition of the energetic material, a misting spray is used inside the reactor to control any dusting that may occur as the energetic material falls through the feed chute into the reactor. Throughout the addition period and the hydrolysis reaction, the caustic solution is vigorously agitated while maintaining the temperature at a desired set point for several hours during which time the energetic materials are completely hydrolyzed. Vigorous agitation is required to ensure that all energetic particles are exposed to complete hydrolysis.

During the hydrolysis reaction, air and liquid samples are taken to monitor the progress of the reaction and quantify the off gassing that occurs. The following process parameters are monitored and recorded continuously throughout the operation:

- Dump Tank Temperature
- Dump Tank Level
- Reactor Head Space Temperature
- Caustic Storage Tank Level
- Acid Storage Tank Level
- Circulation Flow
- Circulation Temp
- Reactor Temperature, Primary
- Reactor Temperature, Redundant
- Circulation Loop Temperature
- Reactor pH
- Building 15-lb. Steam Temperature
- Reactor Water Spray Flow
- Reactor Acid Spray Flow
- Reactor Cooling Water Temperature
- Reactor Agitator Speed AG-1
- Scrubber Fan Speed
- Dump Tank Agitator Speed
- Loss-in-Weight Feeder Speed
- Reactor Overflow Line Pressure
- Steam Condenser Level
- Reactor Level
- Caustic Flow
- Acid Flow
- Water Flow
- Air Flow Into Reactor
- Air Flow To Scrubber
- Circulation Pump Amps

At the conclusion of the hydrolysis reaction, the hydrolysate is allowed to cool to ~35°C. The hydrolysate will be held in the reactor, with continuous agitation, to conduct chemical analysis to characterize the product before releasing to a holding/storage tank to be processed in post-treatment process. If the hydrolysate solution is too alkaline, an acid will be added to control pH to the specified post-treatment process.

The standard operating procedure (SOP) that was developed and validated for the energetics hydrolysis system is in reference 6.

### **3.8 Failure Mode and Effects Analysis (FMEA).**

At the conclusion of the design phase of the program, an FMEA was performed to identify any operational and/or safety issues so that corrective actions could be taken before the reactor system and ancillary hardware was delivered to Holston AAP. Upon receipt and installation of the reactor process system, a second FMEA was performed on the as built/as installed system including all infrastructure support the operation of the hydrolysis system. The results of the two FMEAs are provided in references 7 and 8.

### 3.9 Analysis of Off Gassing.

The off-gas from the reactor was continuously analyzed to determine its composition (see Figure 3-9 for the schematic of the off-gas analysis system and appendix C for a description of the analyses performed by the system).

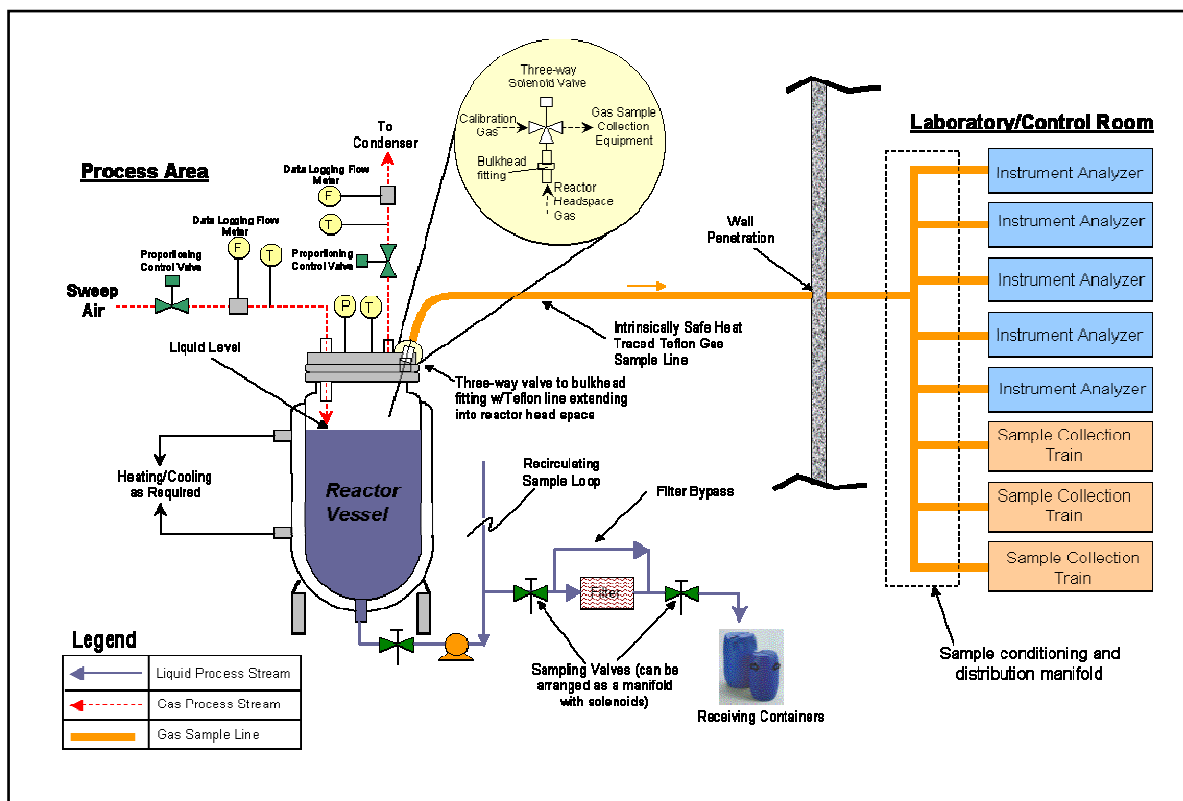


Figure 3-10. Schematic of Off-Gassing Monitoring System (Real Time)

A 1-inch inside diameter Teflon® sample probe is positioned in the gas stream at the exhaust vent of the Reactor Vessel immediately exit of the headspace of the vessel. This probe is connected to three separate Teflon® sample lines approximately 350 feet in length. The lines are steam traced inside the building (about 150 feet) and electrically traced once they exit the restricted area of the building (about 200 feet) and are maintained at approximately 225-250 °F to prevent condensation of moisture (or organic compounds) during transport. The three lines have the following function:

- Line 1: The Batch Train Sample line – ½-inch ID Teflon sample line used to transport approximately 20 Liters/min of headspace gas to the individual batch trains.
- Line 2: The CEMS Sample line – 3/8-inch ID Teflon sample line used to transport approximately 10-15 liters/min of headspace gas to the CEMS analyzers.
- Line 3: The CEMS Calibration line – 3/8-inch ID Teflon sample line used to transport calibration gas from the mobile laboratory to the sample valve and back to the CEMS analyzers in order to calibrate the analytical instruments.

### 3.10 Engineering Design Package.

The engineering design package for the as-installed 2000-gallon hydrolysis reactor and ancillary supporting systems is provided in reference 9.

#### 4.0 MATHCAD™ MODEL & SIMULATION

Of particular interest to the design engineers are the heats of reaction of the individual energetic materials being hydrolyzed. A MathCAD™ model was developed by LANL to estimate the heat released during the hydrolysis of each energetic material and compared to actual lab measurements. The following is extracted from the LANL report:

The heat of reaction was measured using a simple, small-scale, differential-thermal-analysis method. Heat of reaction averaged over the entire run, and heat of reaction at peak reaction temperature. The second is a higher number and should probably be used for safety and design calculations. For reference, similar studies gave the heat of reaction for HMX at 1.5 kJ/g. Other methods for HMX give values of 2.1 and 2.3 kJ/g. Therefore, this method does not give the most conservative answer. The design number should be estimated as 25-35% higher to account for energy loss due to vaporization and/or boiling.

The results using this method had a large amount of variation between samples, and in some cases were difficult to interpret due to foaming and/or boiling problems. However, this data was found useful for a first approximation of the heat liberated during the base hydrolysis reaction. The heat of reaction information, along with previous reaction rate and product information was integrated into a Mathcad™ program to predict products and heat produced during a large-scale hydrolysis run. The information should be used to aid in the scale-up and design of future reactors.

Finally, base hydrolysis data obtained from these two studies was used to determine the thermal runaway temperature threshold for all five explosive and propellants studied. The thermal runaway calculations show that there should be no safety problems if the hydrolysis reactions are run below 130°C. This is well above any temperatures postulated for any atmospheric reactor design.

Table 4-1. Summary of Heats of Reaction

Explosive	NaOH Concentration	$\Delta H_{rxn}$ kJ/g (average) $\pm$ standard deviation	$\Delta H_{rxn}$ kJ/g (peak) $\pm$ standard deviation
M1	12 wt%	0.151 $\pm$ 0.009	0.34 $\pm$ 0.038
M1	20 wt%	0.23 $\pm$ 0.011	0.59 $\pm$ 0.018
M1	35 wt%	0.237 $\pm$ 0.006	1.3 $\pm$ 0.13
M8	12 wt%	Boiled Over for All Flasks	0.94 $\pm$ 0.18
M8	20 wt%	0.228 $\pm$ 0.02	0.89 $\pm$ 0.09
M8	35 wt%	0.211 $\pm$ 0.18	1.39 $\pm$ 0.12
M28	12 wt%	0.115 $\pm$ 0.005	0.35 $\pm$ 0.028
M28	20 wt%	0.12 $\pm$ 0.08	0.38 $\pm$ 0.14
M28	35 wt%	0.38 $\pm$ 0.08	1.06 $\pm$ 0.36
Comp B-4	12 wt%	0.211 $\pm$ 0.006	0.53 $\pm$ 0.041
Comp B-4	20 wt%	0.187 $\pm$ 0.004	0.67 $\pm$ 0.07
Comp B-4	35 wt%	0.34 $\pm$ 0.06	0.90 $\pm$ 0.05
Tetrytol	12 wt%	0.23 $\pm$ 0.05	0.75 $\pm$ 0.07
Tetrytol	20 wt%	0.25 $\pm$ 0.09	0.83 $\pm$ 0.12
Tetrytol	35 wt%	All Flasks Foamed Over	0.81 $\pm$ 0.13

The Mathcad™ simulation model can be used to support scale-up for design purposes so long as the geometry of the reactor remains the same.

## 5.0 PILOT PLANT COMMISSIONING

The energetics hydrolysis system was commissioned using Composition B explosive (nominal composition is 60% RDX {includes HMX percentages varying from 5-20%}, 40% TNT, and plus 1% wax added) to gain operational experience on all unit operations and to verify that the controls and instrumentation was working properly. The working level in the reactor was ~1700-gallons for all commissioning runs, which represented the vendor recommended 80% of reactor volume.

### 5.1 Commissioning Run 1.

Commissioning runs with 200-pounds of Composition B explosive commenced on 14 December 00. Problems were encountered with the Acrison weigh-feeder, which shutdown almost immediately upon starting the feed cycle. Numerous restarts were required before the weigh-feeder would operate. For safety reasons, operators must enter the process area to reset the control panel when the weigh-feeder shuts down – the reset cannot be performed remotely. This problem would recur throughout the commissioning runs, as well as during the test program until the problem could be effectively trouble shoot and corrected.

#### 5.1.1 Weigh-Feeder System:

The shutdown was caused by excessive current draw during the start-up of the drive motor that turns the conditioning and feed augers. The current draw was verified to be correct, peaking at nearly 95% of the maximum. Initially, weight-loading of the energetics on the conditioning and feed augers was thought to be the problem since reducing the amount of explosive in the bin to less than 150 pounds allowed the system to run without the overload at start-up. However, the system was design to handle this amount of weight (and greater weights), and the test program could not be executed efficiently with setting a 150-pound limit on the weigh-feeder. The settings were adjusted to minimize load sensitivity and a high start-up feed rate was used on the recommendation of the vendor. This did not solve the problem but minimized the occurrences, allowing the testing to proceed with minimal schedule delays.

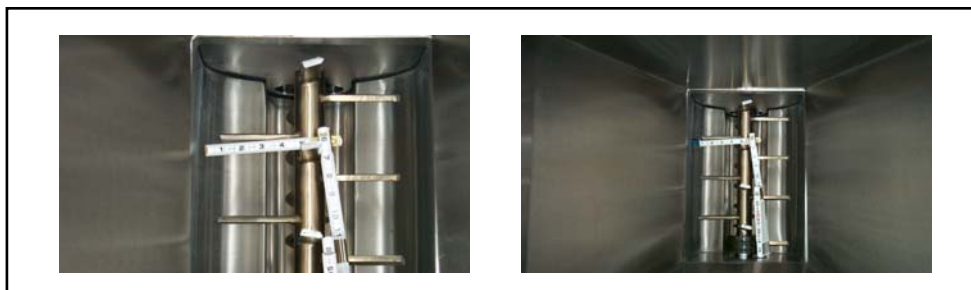


Figure 5-1. Weigh-feeder Modified Conditioning Auger

Finally, through trial and error as the test program proceeded, the conditioning auger design was identified as the cause of the problem. The conditioning auger is used to prevent bridging of the material in the bin. Because energetics are considered non-powdered materials, the vendor selected a blade design. However, the clearances between the blade tips of the conditioning auger and the side-mounted bin tabs were only 0.125-inches. Under certain situations, the energetics would settle in the bin and become trapped between the auger blade and sidewall tab causing an immediate current draw at start-up. (Note: This was not an explosion hazard since the force on the energetics never materialized.) The auger blade was not angled, which further aggravated the problem since the flat blade had to push through the material in the bin, placing a large load on the motor at start-up. The blade should have been slightly angled so as to pass more easily through the material and thereby reducing the load on the motor. The conditioning auger was removed and the auger tips shortened by 0.750-inches increasing the clearance from 0.125 to 0.875-inches. This modification appeared to solve the problem.

### 5.1.2 Test Results:

The plots present Composition B explosive destruction as a function of reactor residence time. Hydrolysate samples were taken during both the addition and the reaction periods. The peaks on the plots show high energetics concentration during the first four hours addition time.

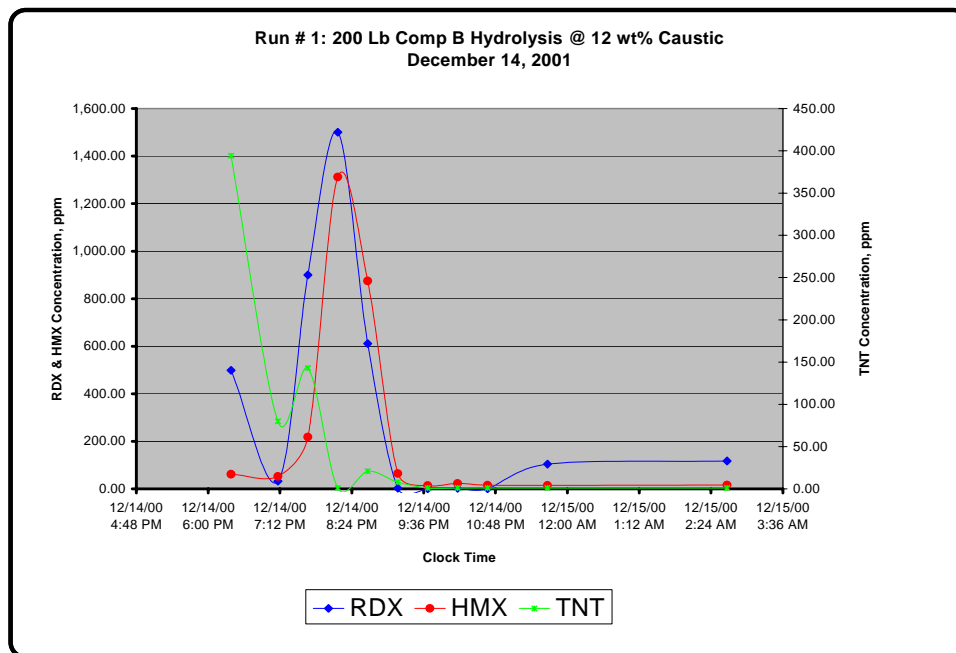


Figure 5-2. Run 1, Mid-Run Destruction Efficiency

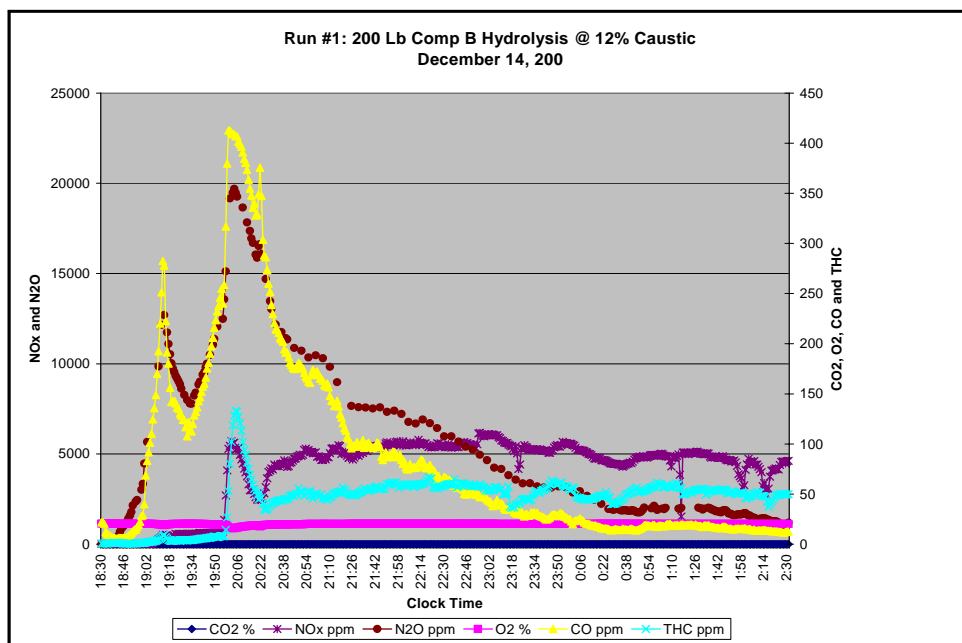


Figure 5-3. Run 1, Off-gas Production

Table 5-1. Run 1, Composition B Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,2-Dichloroethene (total)	5.600		4.800	U	ppbv
1,3,5-Trinitrobenzene	6.130	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	617.000				ug/m <sup>3</sup>
2,4-Dinitrotoluene	45.600				ug/m <sup>3</sup>
2,6-Dinitrotoluene	13.700	MAX			ug/m <sup>3</sup>
2-Butanone	58.400	J	340.000	J	ppbv
4-Amino-2,6-Dinitrotoluene	8.650	MAX			ug/m <sup>3</sup>
Acetaldehyde	599.000		699.000		ug/m <sup>3</sup>
Acetone	828.000		1,820.000		ppbv
Ammonia	372,000.000		3,540,000.000		ug/m <sup>3</sup>
Benzene	38.300		34.900		ppbv
Butanal	81.000		49.200		ug/m <sup>3</sup>
Carbon Dioxide	0.080		0.110		%
Carbon Monoxide	103.000		83.400		ppmv
Chloroform	5.600	U	10.600		ppbv
Crotonaldehyde	2.840	U	59.700		ug/m <sup>3</sup>
Cyanide	0.011	U	0.003	U	ug/m <sup>3</sup>
Cyclohexanone	2,650.000		224.000		ug/m <sup>3</sup>
Decanal	252.000		126.000		ug/m <sup>3</sup>
Dibromochloromethane	12.100	J	4.800	UJ	ppbv
Ethylbenzene	5.600	U	11.600		ppbv
Formaldehyde	1,960.000		7,730.000		ug/m <sup>3</sup>
Hexanal	7.370	J	12.100		ug/m <sup>3</sup>
Methylene Chloride	25.600	J	56.600		ppbv
m-Tolualdehyde	20.300	J	1.730	U	ug/m <sup>3</sup>
Nitrous Oxide	6,934.000		6,132.000		ppmv
Nonanal	92.700		3.030	U	ug/m <sup>3</sup>
NOx	275.000		5,018.000		ppmv
Octanal	3.360	U	50.800		ug/m <sup>3</sup>
Pentanal	1.700	U	50.300		ug/m <sup>3</sup>
Propanal	3.890	U	42.400		ug/m <sup>3</sup>
RDX	22.700	MAX			ug/m <sup>3</sup>
Tetrachloroethene	9.300	J	7.900	J	ppbv
Toluene	13.900	J	1,060.000	J	ppbv
Total Hydrocarbons	4.400		81.200		ppmv
Xylenes	10.900		50.600		ppbv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected



### 5.1.3 Hydrolysate Neutralization:

The plan was to neutralize each batch of hydrolysate before pumping the hydrolysate to the tank farm where it would be stored until disposed of as waste. At the conclusion of Run 1, the neutralization of the hydrolysate was initiated the following day using concentrated sulfuric acid (98+%) introduced through the water spray nozzle at up to 20-gallons per minute. Approximately 10% excess NaOH was in the hydrolysate at the end of the hydrolysis reaction.

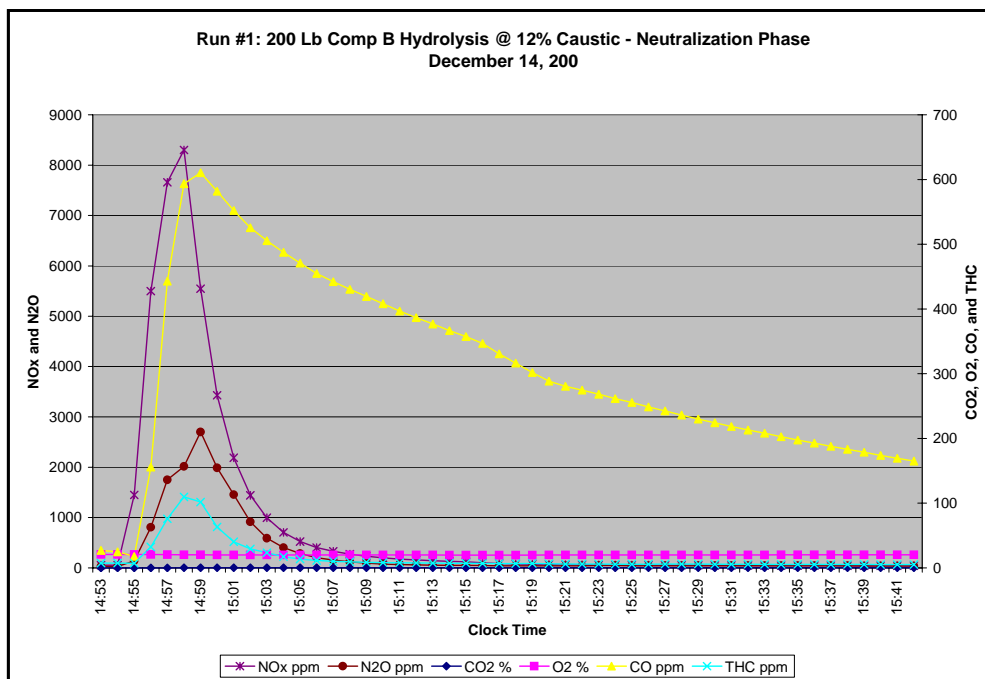


Figure 5-4. Run 1, Composition B Hydrolysate Neutralization Phase

The neutralization reaction is extremely exothermic resulting in an  $\sim 4^{\circ}\text{C}$  temperature rise in  $\sim 4$  minutes, liberating a large amount of NOx and N<sub>2</sub>O that was seen exiting the scrubber exhaust (see Figure 5-4 above). Also, it is possible that even the more stable nitrates / nitrites in the hydrolysate were decomposed at the interface where the acid is being added (rapid pH change combined with highly localized heating, probably flash-boiling; with  $>>100^{\circ}\text{C}$  for a split-split-second).

The neutralization effort was aborted when the acid feed pumped failed (the failure was unrelated to the neutralization process). To avoid schedule delays, it was decided to store the hydrolysates until the testing was completed and equipment improvements could be implemented to the acid feed system to better distribute the acid, and to the scrubber system to handle the NOx emissions. The neutralization would be conducted in bulk at the end of the test and evaluation program. This decision ultimately proved to be a fortuitous since the hydrolysates produced during the test and evaluation program would now be required to support the SCWO testing at DPG.

Neutralization would not normally be performed in the chemical agent disposal facilities since the energetic hydrolysate would proceed to the final treatment step. Furthermore, maintaining the hydrolysate at a pH greater than 9 is important. The hydrolysates, if neutralized to a pH of 4 or lower, will off-gas quite vigorously. This is attributed to the large amounts of sodium nitrite and nitrate in the solution that can be decomposed in the presence of strong mineral acids, such as sulfuric or nitric acids.

#### 5.1.4 Temperature Control – Reactor Cooling Jacket:

While the cooling capacity of the heat exchanger system was more than adequate to handle the exothermic hydrolysis reaction, the temperature control system for the jacket heat exchanger did not perform satisfactory. The control loop cycled between extremes of demanding full cooling to demanding full heating resulting in over-shooting and under-shooting the set point (87°C). This came as a surprise since controlling to a set point should not have presented any challenges to the software. Evidently, the control philosophy was flawed in the sense that there were no dampening features as the actual temperature approach the set-point temperature. As a result, the temperature of the jacket was controlled manually through the control panel.

#### 5.1.5 Mass Flow Meter:

The mass flow meter was installed to monitor changes in the fluid properties of the hydrolysate as the hydrolysis reaction proceeded to conclusion. The meter was installed on the suction side of the recycle pump. The meter performed acceptable during equipment debug and set-up (water and caustic solution). Shortly after the addition of the Composition B explosive was initiated, the meter reading went off-scale, initially leading the operators to believe that the recycle line had become clogged. However, the current draw on the recycle pump was normal, and there was no temperature change in the loop. After the addition of the Composition B was completed, and the hydrolysis reaction had been under way for 6 hours, the readings on the mass flow meter returned.

The cause of the meter malfunction was aeration of the suction side of the recirculation loop and the off-gassing taking place from the hydrolysate solution during the digesting of the explosive. The mass flow meter should have been installed on the discharge side of the line, and a de-aerating device installed in the line to protect the meter. This failure occurred again on Runs 2 and 3. The aggressive schedule did not allow time to correct the problem before testing was concluded for the program. While the failure of the mass flow meter did not impact the processing studies, the opportunity to obtain “nice to have” information regarding the characterization of changes in fluid viscosity as the reaction proceed with different caustic strength and energetic loadings was lost.

## 5.2 Commissioning Run 2.

Commissioning Run 2 was conducted with Composition B explosive fed at a measured rate of up to 492 lbs/hr to the reactor – the maximum rate anticipated for energetics in a full-scale chemical weapon demilitarization facility. Based on experiences of Run 1, the jacket temperature was manually controlled and liquid samples would again be taken during the explosive addition. The same feeder problems occurred as were encountered on Run 1. The mass flow meter malfunctioned shortly after the addition of the explosive was initiated, confirming believe that the recycle line was aerating, and possible off gassing of energetics was taken place in the recycle line as the hydrolysate flowed through the pipe.

### 5.2.1 Test Results:

The following charts plot the destruction of the Composition B explosive. Figure 5-5 tracks the destruction of the Composition B explosive against time.

The significant rise and fall of the HMX and RDX concentrations shown is probably the result of HMX and RDX being freed from the TNT as the TNT is being melted and hydrolyzed, and then entering the recycle line as the hydrolysis proceeds to conclusion. This became the typical cyclic trace for all samples taken during the addition process.

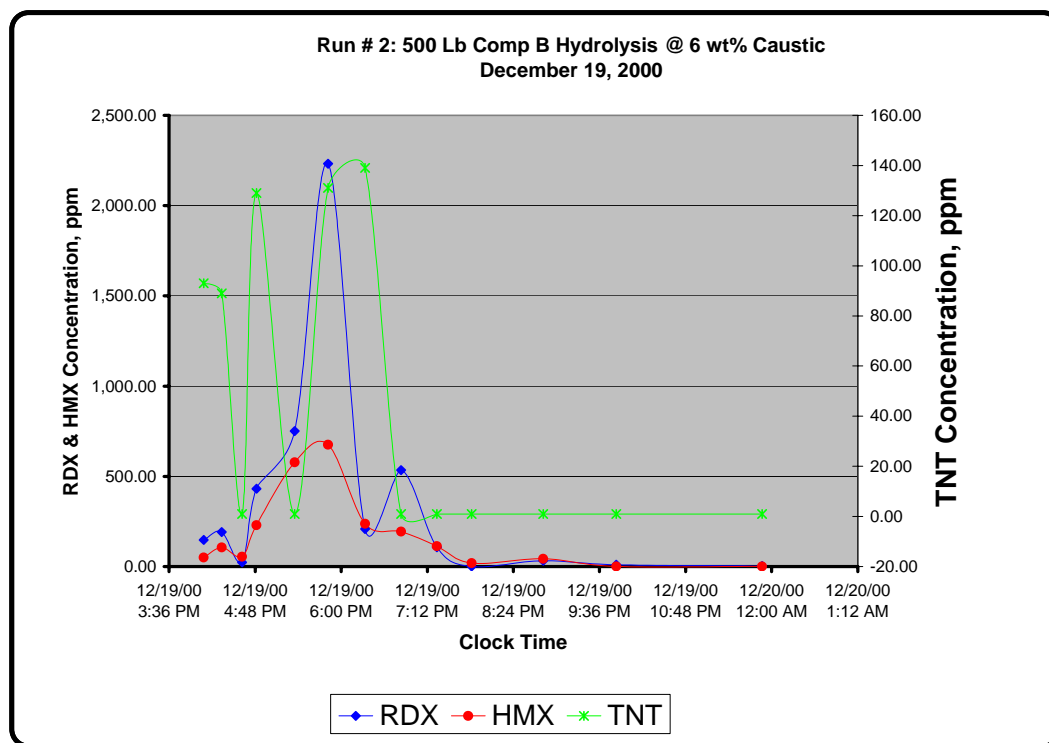


Figure 5-5. Run 2, Mid-Run Destruction Efficiency

Figure 5-6 shows the off gassing that was occurring during the hydrolysis reaction. The repeated stopping and starting of the weigh-feeder as the operators struggle to keep the feed system operating caused the multiple spikes in the traces for NO<sub>x</sub>, N<sub>2</sub>O and CO. The off gassing rate decreased when the feeder stopped, and as soon as the feeder was restarted the off gassing rate increased.

Although unintentional, this shows how closely the off gassing tracked with the rate of energetics addition and the destruction of the energetic.

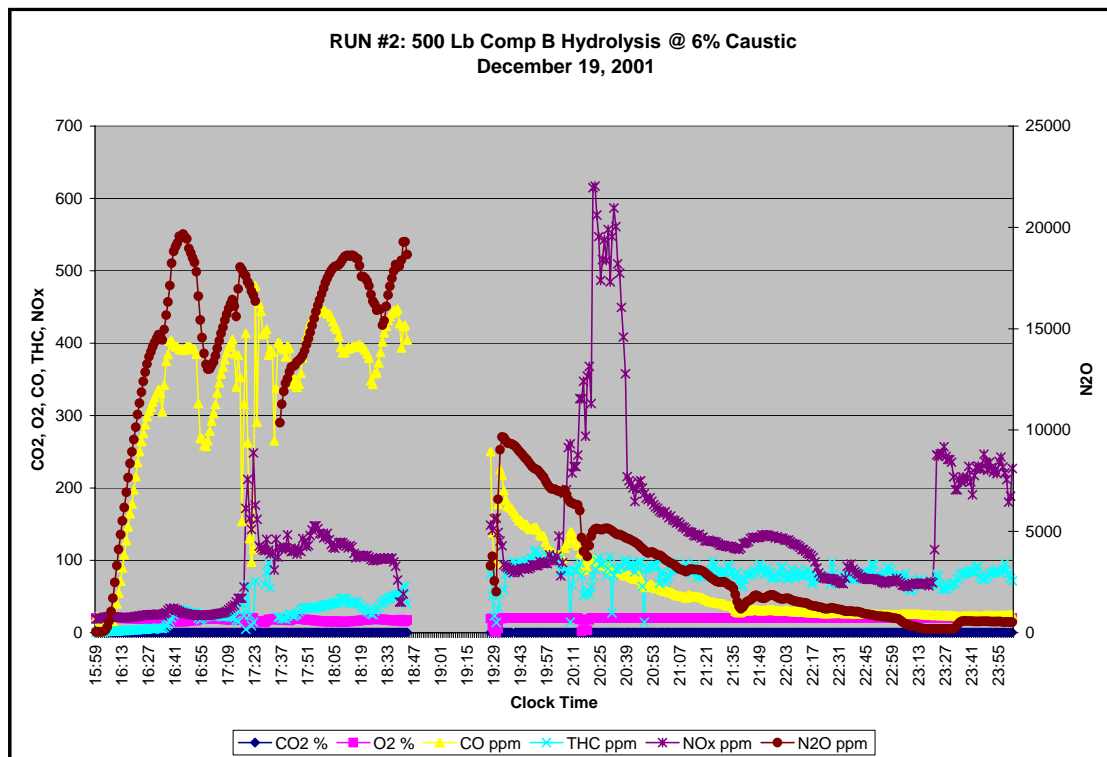


Figure 5-6. Run 2, Off-gas Production

During Run 2, severe foaming was encountered that eventually contaminated the air sampling lines. The agitation in the reactor was increased to bring the foam under control, indicated by the spiking of the NO<sub>x</sub> trace. The foaming problem was aggravated because the level within the reactor was extremely high – at least 18-inches above the upper agitator, consequently, the vortex was nearly non-existent. The additional water entering the reactor through the spray nozzle used to prevent dusting of the explosive as the explosive fell into the reactor caused the high level.

Run 2 was the last run conducted in calendar year 00. Testing was not resumed until February 01. TRC took the break in testing as an opportunity to clean the sampling lines, which were contaminated by the foaming and particle deposition. The lines were flushed using DI water and solvent followed by a nitrogen purge. The Teflon probe was increased from 0.375-inches diameter to 1.0-inch diameter.

The concentration of the major components of the off gas stream is provided in Table 5-2.

Table 5-2. Run 2, Composition B Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	18.20	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	3,140.00				ug/m <sup>3</sup>
2,4-Dinitrotoluene	314.00	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	2,730.00				ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	148.00	MAX			ug/m <sup>3</sup>
Acetaldehyde	595.00	J	1,120.00	J	ug/m <sup>3</sup>
Ammonia	1,580,000.00		12,000,000.00		ug/m <sup>3</sup>
Benzene	45.70		35.40		ppbv
Butanal	0.39	UJ	2.63	UJ	ug/m <sup>3</sup>
Carbon Dioxide	0.05		0.07		%
Carbon Monoxide	313.40		55.60		ppmv
Crotonaldehyde	250.00	J	401.00	J	ug/m <sup>3</sup>
Cyanide	0.01		0.30		ug/m <sup>3</sup>
Cyclohexanone	1.21	UJ	8.29	UJ	ug/m <sup>3</sup>
Decanal	227.00	J	60.50	UJ	ug/m <sup>3</sup>
Dibromochloromethane	13.20		17.50	U	ppbv
Formaldehyde	137,000.00	J	749,000.00	J	ug/m <sup>3</sup>
Hexanal	237.00	J	7.76	UJ	ug/m <sup>3</sup>
HMX	1,180.00	MAX			ug/m <sup>3</sup>
Methylene Chloride	22.60		26.30	U	ppbv
m-Tolualdehyde	2.87	UJ	288.00	J	ug/m <sup>3</sup>
Nitrous Oxide	17,015.00		3,686.00		ppmv
Nonanal	5.03	UJ	34.30	UJ	ug/m <sup>3</sup>
NOx	37.10		146.20		ppmv
Octanal	2.04	UJ	13.09	UJ	ug/m <sup>3</sup>
Pentanal	2,350.00	J	1,290.00	J	ug/m <sup>3</sup>
Propanal	2.35	UJ	408.00	J	ug/m <sup>3</sup>
RDX	31,500.00				ug/m <sup>3</sup>
Total Hydrocarbons	32.80		101.20		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

### 5.2.2 Foaming:

Foaming was a problem at PANTEX during the processing of Composition B and Tetrytol explosives. The major concern other than over-flowing the reactor is trapping heat from the exothermic reaction in the hydrolysate solution. The foam is an excellent insulator and, if covering the entire liquid surface will trap heat being carried from the solution by the evolved gasses.

Foaming was encountered in all of the commissioning runs. During Run 2, the foam accumulated to a depth of nearly 12-inches and was ejected from the reactor through the reactor air vent. The water spray was inadequate to control the foaming. The foaming is attributed to the gases that are produced by hydrolysis of the HMX and RDX. The TNT decomposes into polymers forming an organic phase that is lighter than the base solution, which rises to the top of the liquid. This organic layer prevents the free flow of any gases formed from the decomposition of the RDX/HMX. The gas then forms foam as it escapes through the organic layer. This surface layer of foam can be broken-up through rapid mixing or by using an anti-foaming agent (ref. 10), allowing the gas to freely escape the hydrolysate solution.



Figure 5-7. Agitation within the Hydrolysis Reactor (Vortex Formation)

The foaming was controlled during the commissioning runs by adjusting agitator speed when a build-up of foam was detected by the level sensor (the level sensor would report a level in the reactor that did not match with the calculated level based on the amount of caustic and water introduced to the reactor). Ultimately, foaming was controlled by adjusting the operating level of the hydrolysate within the reactor relative to the location of the vortex generated by the agitator blades. So long as a clearly defined vortex was maintained in the reactor, any foam formed during the hydrolysis would be quickly drawn below the surface and dissipated. Figure 5-7 shows the vortex formed by the upper agitator blade assembly (water). Controlling the level within the reactor relative to the vortex solved the problem of controlling foaming.

### 5.2.3 Overflow Incident:

On the morning after the completion of Run 2, the software defaults were accidentally “pasted over” during on-line programming that was being performed by the subcontractor. This caused the water

valve to the reactor to open and overflow the hydrolysate into the dump tank that was provided for such situation (see the FEMA). The overflow, caused by human error, was contained in the dump tank (3000-gallons of water was introduced to the reactor before the error was identified and the water valve closed).



Figure 5-8. Secondary Containment "Dump" Tank

However, some of the hydrolysate overflowed the reactor escaping through the water seal. This hydrolysate was contained by the secondary containment dike about the reactor and directed to the dump tank. This incident indicated that a packing gland seal on the agitator shaft, which would have prevented the hydrolysate from escaping the reactor, should replace the water seal. This was the only incident to occur during the commissioning or test and evaluation runs that resulted in an unintentional release of hydrolysate (confined by the secondary containment system).

### 5.3 Commissioning Runs 3 through 5.

Working at ~80% reactor volume presented problems in terms of caustic consumption and operating efficiency. Therefore, it was decided to conduct Runs 3-5 in increments as follows:

Run 3 was conducted with 20% caustic strength. Approximately 250 pounds of explosive was fed over a 2-hour period – a nominal rate of 125 lbs/hr. The starting volume was approximately 1,700-gallons.

Run 4 was conducted using the hydrolysate produced in Run 3. The adjusted caustic strength was 14%. An additional 500 pounds of Composition B explosive was fed into the hydrolysate solution at a rate of 125 lbs/hr (4-hour addition period).

Run 5 was conducted using the combined hydrolysate produced during Runs 3 and 4 as the starting solution. The caustic strength in the hydrolysate was 9.6%. An additional 500 pounds of Composition B explosive was fed into the hydrolysate solution at a rate of 500 lbs/hr.

This approach conserved caustic, minimized the amount of hydrolysis produced (waste disposal was an issue at this point in the program), maximize use of the reactor, and provide insight into a process where energetics is continuously added to a “heal” of hydrolysate of diminishing caustic strength.

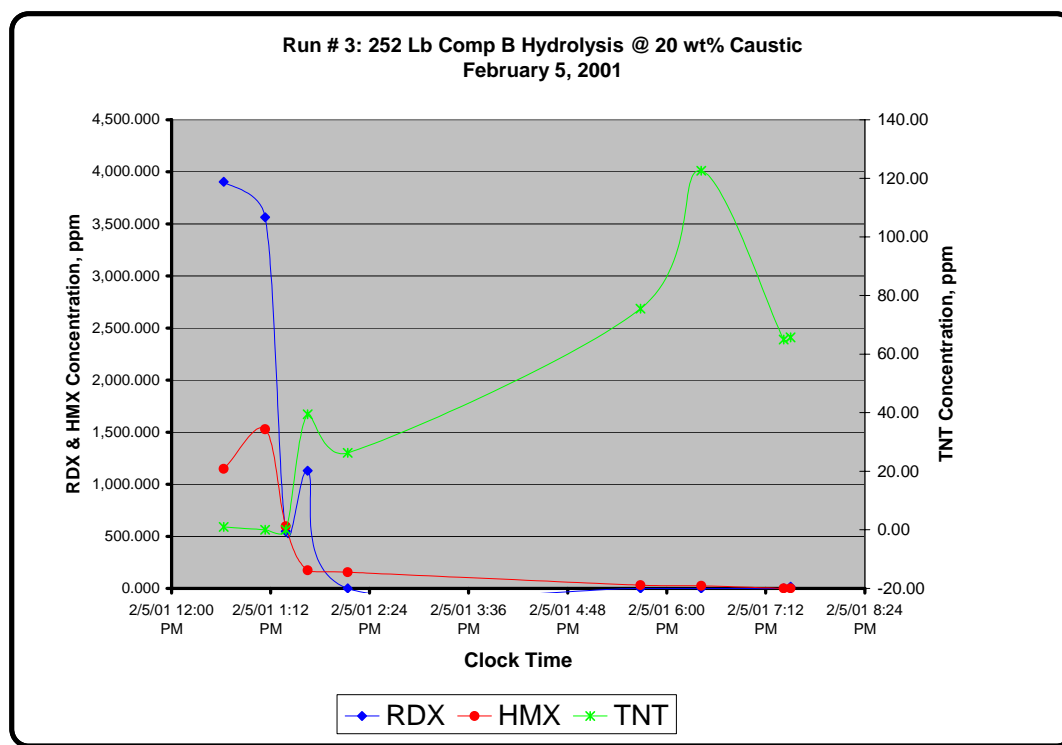


Figure 5-9. Run 3, Mid-Run Destruction Efficiency for Composition B



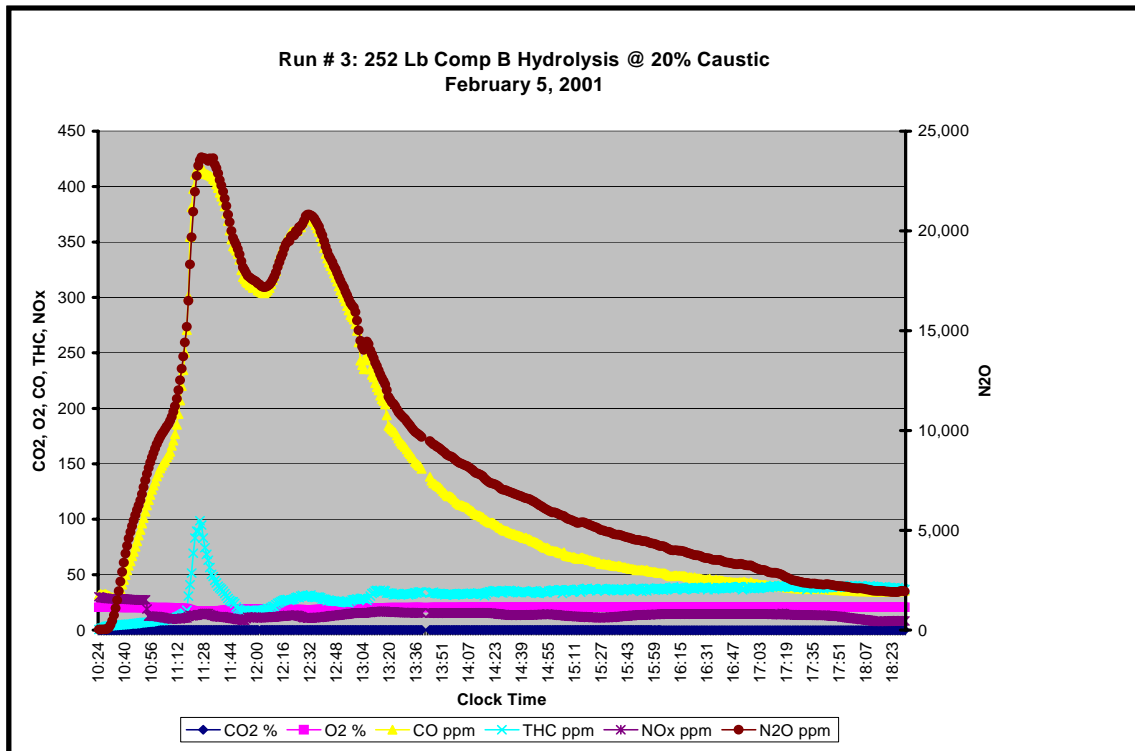


Figure 5-10. Run 3, Off-gas Production for Composition B

Table 5-3. Run 3, Composition B End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	1,380.00	mg/l	1,380.00	
Aluminum	9,490.00	mg/l	9,490.00	
Ammonia	1,050.00	mg/l	1,050.00	
Beryllium	2,200.00	mg/l	2,200.00	
Calcium	16,420.00	ug/l	16.42	
Chromium	12,790.00	ug/l	12.79	
Copper	90,900.00	ug/l	90.90	
Cyanide (Sodium Cyanide)	1,710.00	ug/l	1.71	
Fluoride	2,320.00	ug/l	2.32	
Formate	86,100,000.00	ug/l	86,100.00	
HMX	15,800.00	ug/l	15.80	
Iron	230.00	mg/l	230.00	J
Lead	5.90	ug/l	0.01	J
Magnesium	1,000.00	ug/l	1.00	J
Mercury	2.20	ug/l	0.00	J
Nitrite-N	13,000.00	ug/l	13.00	J
Sodium	210.00	ug/l	0.21	J
TNT	430.00	ug/l	0.43	J
Zinc	3,700.00	ug/l	3.70	J
TIC	684.25	mg/l	684.25	
TOC	7,171.00	mg/l	7,171.00	
COD	18,900.00	mg/l	18,900.00	
Total Suspended Solids	840.00	mg/l	840.00	J
Total Dissolved Solids	201,000.00	mg/l	201,000.00	
Normality as NaOH	7.50	n		
Density	1.15	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 5-4. Run 3, Composition B Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
2,4,6-Trinitrotoluene	3,370.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	88.60	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	31.90	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	119.00	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	150.00	MAX			ug/m <sup>3</sup>
Acetaldehyde	311.00		20.60		ug/m <sup>3</sup>
Acetone	414.00		1,140.00		ppbv
Ammonia	3,570,000.00		4,920,000.00		ug/m <sup>3</sup>
Butanal	43.60		15.30		ug/m <sup>3</sup>
Carbon Dioxide	0.09		0.05		%
Carbon Disulfide	26.80		35.20		ppbv
Carbon Monoxide	216.00		62.00		ppmv
Chloroform	27.80				ppbv
Crotonaldehyde	4.71	J	0.86	J	ug/m <sup>3</sup>
Cyclohexanone	1,760.00		31.60		ug/m <sup>3</sup>
Decanal	387.00		40.90		ug/m <sup>3</sup>
Dibromochloromethane	12.50		10.00	U	ppbv
Formaldehyde	3,590.00	D	144.00		ug/m <sup>3</sup>
Heptanal	29.40		1.12	U	ug/m <sup>3</sup>
Hexanal	39.80		2.84	J	ug/m <sup>3</sup>
HMX	28.90	MAX			ug/m <sup>3</sup>
Methylene Chloride	54.30	B	113.00	B	ppbv
m-Tolualdehyde	13.80				ug/m <sup>3</sup>
Nitrous Oxide	13,875.00		6,784.00		ppmv
Nonanal	32.50				ug/m <sup>3</sup>
NOx	0.00		0.00		ppmv
Octanal	37.10				ug/m <sup>3</sup>
Oxygen	19.50		20.70		%
Propanal	288.00		24.80		ug/m <sup>3</sup>
RDX	2,220.00	MAX			ug/m <sup>3</sup>
Toluene			12.50		ppbv
Total Hydrocarbons	31.00		45.10		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

D = Result was obtained from analysis of a dilution or surrogate were diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

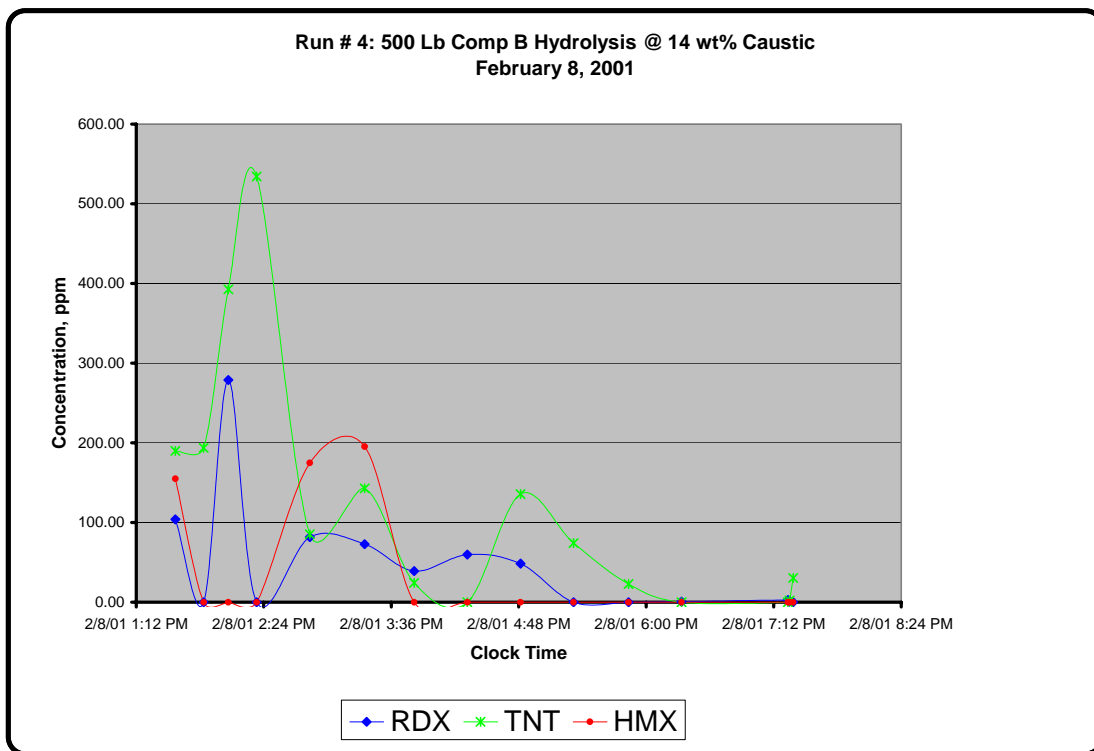


Figure 5-11. Run 4, Mid-Run Destruction Efficiency for Composition B

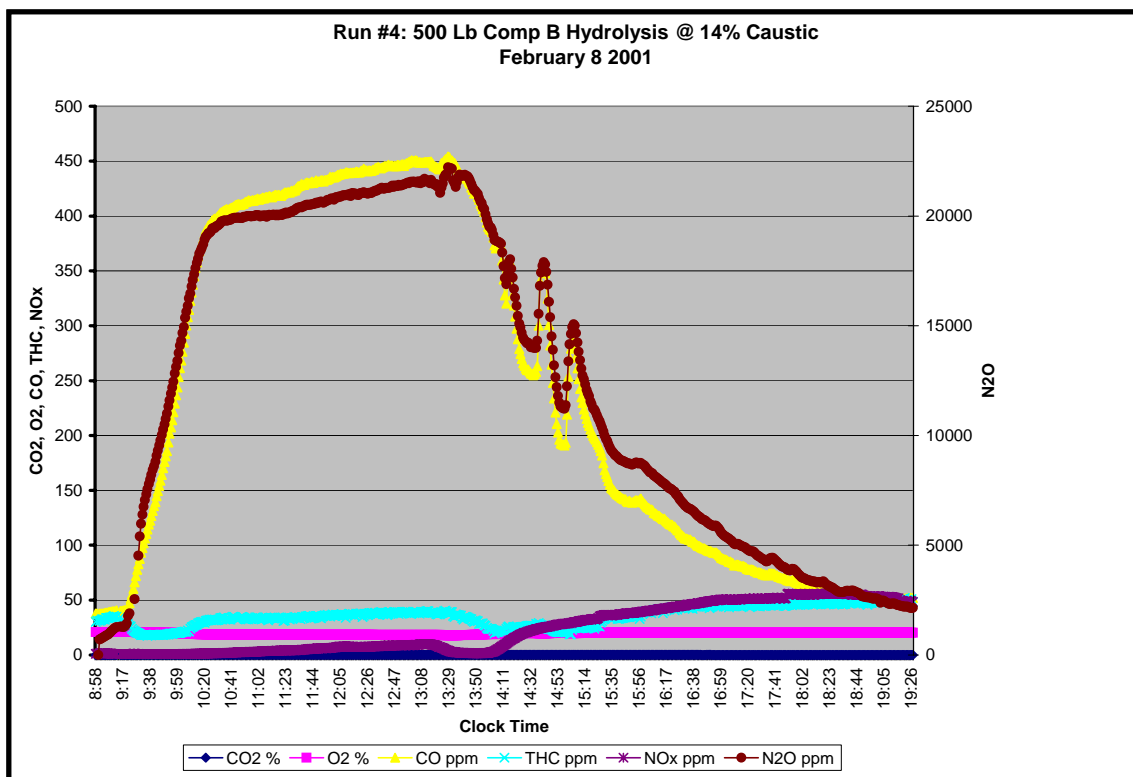


Figure 5-12. Run 4, Off-gas Production for Composition B

Table 5-5. Run 4, Composition B End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	3,010.00	mg/l	3,010.00	
Aluminum	960.00	ug/l	0.96	J
Ammonia	2,540.00	mg/l	2,540.00	
Beryllium	2.60	ug/l	0.0026	J
Calcium	16,000.00	ug/l	16	J
Chromium	230.00	ug/l	0.23	J
Cobalt	150.00	ug/l	0.15	J
Copper	440.00	ug/l	0.44	J
Cyanide (Sodium Cyanide)	40,100.00	ug/l	40.1	
Fluoride	260.00	mg/l	260.00	J
Formate	20,200.00	mg/l	20,200.00	
Iron	3,000.00	ug/l	3	J
Lead	530.00	ug/l	0.53	J
Magnesium	4,210.00	ug/l	4.21	
Manganese	69.00	ug/l	0.069	J
Nitrite-N	5,100.00	mg/l	5,100.00	
Phosphorus	530.00	ug/l	0.53	J
Potassium	22,000.00	ug/l	22	J
Silver	59.00	ug/l	0.059	J
Sodium	68,900,000.00	ug/l	68900	
TNT	2,720.00	ug/l	2.72	
Zinc	8,980.00	ug/l	8.98	
TIC	1,380.00	mg/l	1,380.00	
TOC	17,537.50	mg/l	17,537.50	
COD	41,400.00	mg/l	41,400.00	
Total Dissolved Solids	187,000.00	mg/l	187,000.00	
Total Suspended Solids	164.00	mg/l	164.00	
Normality as NaOH	4.25	n		
Density	1.12	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 5-6. Run 4, Composition B Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5- Trinitrobenzene	37.30	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	3.65	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	6710.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	124.00	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	33.60	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	37.30	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	57.40	MAX			ug/m <sup>3</sup>
Acetaldehyde	1350.00		69.10		ug/m <sup>3</sup>
Acetone	552.00		404.00		ppbv
Ammonia	4110000.00		16,200,000.00		ug/m <sup>3</sup>
Bromodichloroethane	20.00		13.80	U	ppbv
Butanal	87.70		29.70		ug/m <sup>3</sup>
Carbon Dioxide	0.12		0.07		%
Carbon Monoxide	323.00		123.00		ppmv
Chloroform	16.10		13.80	U	ppbv
Crotonaldehyde	14.80		0.56	U	ug/m <sup>3</sup>
Cyanide	0.01		0.01		ug/m <sup>3</sup>
Cyclohexanone	6260.00	D	278.00		ug/m <sup>3</sup>
Decanal	619.00		175.00		ug/m <sup>3</sup>
Dibromochloromethane	20.50		13.80	U	ppbv
Formaldehyde	6870.00	D	347.00		ug/m <sup>3</sup>
Heptanal	34.60		21.00		ug/m <sup>3</sup>
Hexanal	40.00		29.10		ug/m <sup>3</sup>
HMX	16.20	MAX			ug/m <sup>3</sup>
Methylene Chloride	73.30	B	90.90	B	ppbv
m-Tolualdehyde	0.36	J	13.00		ug/m <sup>3</sup>
Nitrous Oxide	18089.00		9,180.00		ppmv
Nonanal	47.10		22.60		ug/m <sup>3</sup>
NOx	0.00		16.80		ppmv
Octanal	50.10		23.80		ug/m <sup>3</sup>
Oxygen	18.90		20.00		%
Propanal	454.00		83.30		ug/m <sup>3</sup>
RDX	3,690.00	MAX			ug/m <sup>3</sup>
Toluene	12.70		13.80	U	ppbv
Total Hydrocarbons	42.60		47.90		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

D = Result was obtained from analysis of a dilution or surrogate were diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

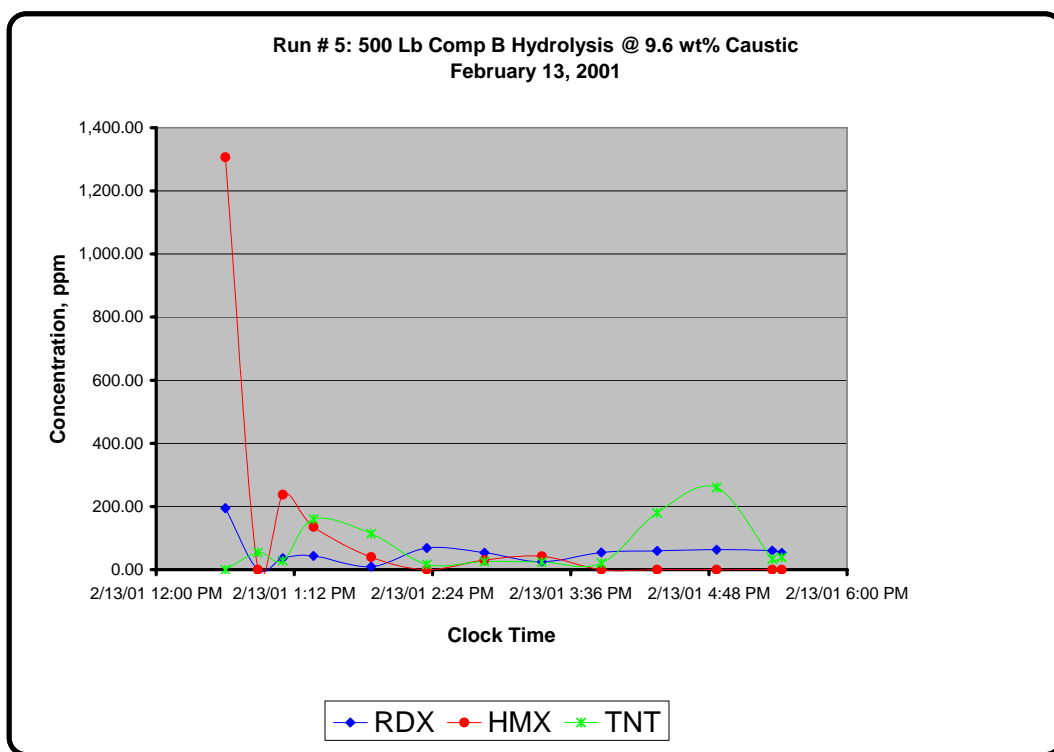


Figure 5-13. Run 5, Mid-Run Destruction Efficiency for Composition B

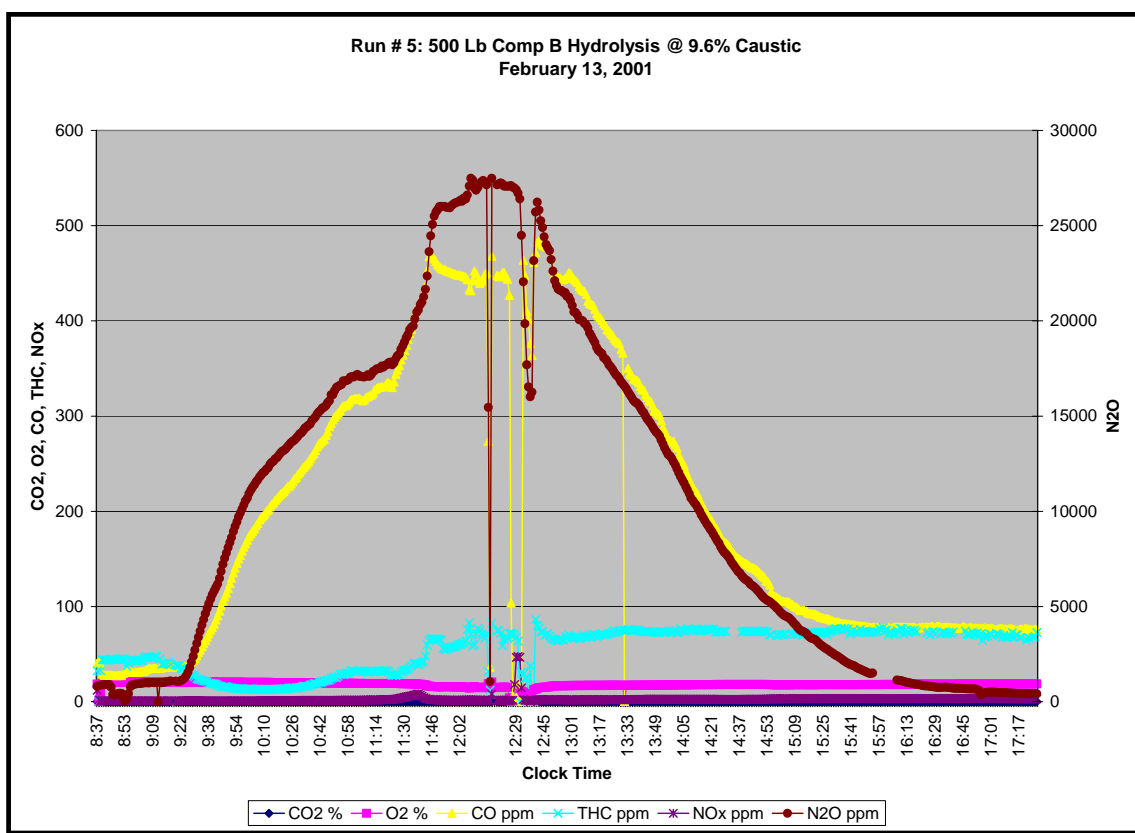


Figure 5-14. Run 5, Off-gas Production for Composition

Table 5-7. Run 5, Composition B End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	3,680.00	mg/l	3,680.00	
Aluminum	1300	ug/l	1.30	J
Ammonia	1,380.00	mg/l	1,380.00	
Beryllium	3.8	ug/l	0.00	J
Calcium	24000	ug/l	24.00	J
Chromium	160	ug/l	0.16	J
Cobalt	200	ug/l	0.20	J
Copper	380	ug/l	0.38	J
Cyanide (Sodium Cyanide)	40,000.00	ug/l	40.00	
Formate	27,600.00	mg/l	27,600.00	
Iron	2700	ug/l	2.70	J
Lead	670	ug/l	0.67	J
Magnesium	5,920.00	ug/l	5.92	
Nitrite-N	123.00	mg/l	123.00	
Silver	85	ug/l	0.09	J
Sodium	62,200,000.00	ug/l	62,200.00	
Sulfate	149.00	mg/l	149.00	
TNT	24,940.00	ug/l	24.94	
Zinc	3,880.00	ug/l	3.88	
TIC	1,917.50	mg/l	1,917.50	
TOC	21,190.00	mg/l	21,190.00	
COD	56,000.00	mg/l	56,000.00	
Total Suspended Solids	170.00	mg/l	170.00	
Total Dissolved Solids	176,000.00	mg/l	176,000.00	
Normality as NaOH	1.15	n		
Density	1.12	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 5-8. Run 5, Composition B Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,1,2,2-Tetrachloroethane	6.00	U	8.80		ppbv
1,3,5- Trinitrobenzene	7.14	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	1.61	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	1,710.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	40.80	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	10.70	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	23.20	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	33.30	MAX			ug/m <sup>3</sup>
Acetaldehyde	442.00		78.40		ug/m <sup>3</sup>
Acetone	6.00	U	262.00		ppbv
Acetonitrile	482.50	J	4,651.15	J	ppbv
Ammonia	8,780,000.00		82,300,000.00		ug/m <sup>3</sup>
Benzene	6.00	U	33.30		ppbv
Bromodichloroethane	28.70		8.80	U	ppbv
Butanal	46.70		42.80		ug/m <sup>3</sup>
Carbon Dioxide	0.09		0.04		%
Carbon Monoxide	238.00		153.00		ppmv
Chloroform	23.60		8.80	U	ppbv
Crotonaldehyde	1.01	J	0.78	U	ug/m <sup>3</sup>
Cyanide	0.00	U	0.04		ug/m <sup>3</sup>
Cyclohexanone	3,710.00		33.10		ug/m <sup>3</sup>
Decanal	164.00		44.90		ug/m <sup>3</sup>
Dibromochloromethane	27.00		8.80	U	ppbv
Formaldehyde	1,720.00		142.00		ug/m <sup>3</sup>
HMX	9.25	MAX			ug/m <sup>3</sup>
Methylene Chloride	44.30	B	97.20	B	ppbv
m-Tolualdehyde	0.89	J	8.30		ug/m <sup>3</sup>
Nitrous Oxide	15459.00		9,078.00		ppmv
Nonanal	51.20		31.40		ug/m <sup>3</sup>
NOx	1.30		2.30		ppmv
Octanal	52.50		37.00		ug/m <sup>3</sup>
Oxygen	19.20		18.00		%
RDX	403.00	MAX			ug/m <sup>3</sup>
Silanol, trimethyl-			221.79	J	ppbv
Toluene	4.74		8.80	U	ppbv
Total Hydrocarbons	40.70		113.80		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

D = Result was obtained from analysis of a dilution or surrogate were diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank



### 5.3.1 Spray Nozzle:

The original Teflon spray nozzle with rotating head provided by Pfaudler to control dusting during the energetics addition did not perform very well; the water droplets generated were too large to be effective and the flow rate was too high (about 20 gpm), adding a significant volume of water to the hydrolysate and raising the water level within the reactor. The spray nozzle was used sparingly during Runs 3 through 5, and the spray nozzle assembly was redesigned before proceeding with the test runs.

RONA's solution for the spray nozzle was to fabricate a 1.5-inch diameter stainless steel pipe, which was welded closed on the end and equipped with three fixed spray nozzles (McMaster Carr Catalog 106 (Stock # 32815K52)) on the outside of the pipe. Each nozzle had a flow rate of 0.38 gpm, which correlated to an approximate total flow rate of 1.2 gpm. The nozzles were very effective in providing a "fine mist" spray. The nozzles were oriented to provide a "horizontal" stream of the mist spray that covered the entire surface of the vessel. In other words, a blanket or cloud of mist would cover the surface of the hydrolysate (and in some cases foam). The resulting droplets hitting the surface of the hydrolysate were effective in "breaking up" and controlling the foam (when combined with high agitation, which created a reasonably strong vortex).

### 5.3.2 Discussion of Commissioning Results:

The commissioning runs indicated that the system could be operated safely and efficiently, and that the formal test program could commence. Many equipment improvements were identified that would be implemented as the program proceeded (or at a later date) with the caveat that these improvements did not delay the test schedule. Some of the areas identified included:

- Replace agitator water seal with a packing gland or rotary seal
- Develop a software logic to link the level detector output to water and caustic totalizers to simplify the identification of foaming
- Improved NO scrubbing capabilities including auto-emissions detection linked to the PC software
- Heat exchanger programming for accurate temperature control of the set point
- Water and caustic preheating to shorten start-up time
- Feeding of energetics in slurry form to increase throughput and simplify handling

The results of the liquid analyses performed at the Holston AAP laboratory confirmed that the Composition B explosive was destroyed to below the DRE goal of 99.999%.

The ups and downs in the concentration of the energetics during mid run sampling and analysis for Runs 3 through 5 is most likely due to the fact that some energetic particles are entering and passing through the recycle loop where the samples are being collected by the auto-sampler system. The important thing is that at the end of the run there are no energetic materials in the hydrolysate and if there are some, the concentration is very low. Please note: it is not easy to draw a liquid sample from a 2,000-gallon dynamic reactor and have a representative sample of the reactor content.

During the off gas stream characterization of Runs 3 through 5, it was revealed that some energetic materials (TNT, DNT, RDX, HMX, 1,3,5 - Trinitrobenzene) are present during the addition of energetics and disappeared once addition is completed. TNT and DNT have measurable vapor pressures at ambient temperatures; therefore, one would expect these materials to be included in the off-gassing stream. The presence of RDX and HMX in the gas stream is most likely contributed to the fact these materials are entrained in water droplets in the off gas stream. Also, some dusting occurs as the energetic materials fall into the reactor through the headspace air stream, possibly contributing to these readings. Use of a condenser, just above the reactor, and a water-mister to drop any entrained materials back into the reactor should be effective in confining these materials to within the reactor system.

The inorganic materials (metals) detected in the hydrolysate end of runs analysis are sourced from the sodium hydroxide stock feed that contains some of these components.

## 6.0 ENERGETICS HYDROLYSIS TESTS

The tests conditions for the following energetics were established to determine the optimum caustic soda concentration, which will insure maximum destruction efficiency (< 99.999%) at a minimum reactor residence time.

<u>Composition B4 Explosive</u>	Nominal composition is 59.75% RDX (includes HMX percentages varying from 5-20%), 39.75% TNT, and 0.50% calcium silicate
<u>M1 Propellant</u>	Nominal composition is 84% nitrocellulose, 9% Dinitrotoluene, 5% dibutylphthalate, 1% diphenylamine, and 1% lead carbonate
<u>M8 propellant (sheet)</u>	Nominal composition is 52.15% nitrocellulose, 43% nitroglycerin, 3% diethylphthalate, 1.25% potassium nitrate, and 0.60% ethyl centralite
<u>Tetrytol Explosive</u>	Nominal composition is 70% Tetryl and 30% TNT
<u>M28 Propellant (granular)</u>	Nominal composition is 60% nitrocellulose, 23.8% nitroglycerin, 9.9% triacetin, 2.6% dimethylphthalate, and 2.0% lead stearate, and 1.7% 2-nitrodiphenylamine

In addition, a mixture of M28 leaded propellant and Composition B4 explosive (86/14 weight-percent based on their amount/ratio in the 115-mm Rocket, Chemical Agent VX, M55) was hydrolyzed to address NRC concerns.

It is also the objective of these runs to fully characterize the hydrolysate by-product and off-gas during energetic hydrolysis and at the end of the each run.

The tests were conducted at 12-, 20- and 25-weight percent caustic strength and at a nominal feed rate of: 1<sup>st</sup> hour - 50 lbs. hour; 2<sup>nd</sup> hour - 100 lbs. per hour; 3<sup>rd</sup> hour - 150 lbs. per hour; 4<sup>th</sup> hour - 200 lbs. per hour for a total processed weight of 500 pounds (unless otherwise stated in the respective tables).

To minimize the amount of caustic consumed during the tests, the operating level within the reactor was set just above the lower agitator blade; a volume equivalent to approximately 700-gallons.

Tests were not combined (i.e., the hydrolysate from one test was not carried over to the next test) to ensure that the liquid analyses and off-gassing profiles were unique to the respective caustic solution strength, and so as not to have residuals compounds from a previous test possibly effect the results of the current test. The tests were structured in this manner to examine the effect the various feed rates and caustic strengths had on evolved gasses, rate of reaction, by-products, etc.

The hydrolysate analysis and data collection was performed after completion of the 4-hour addition time unless otherwise specified. The off-gas analysis and data collection was performed from the beginning of the run.

The Test Plan Requirements are provided in reference 11.

## 6.1 Composition B4 Explosive Hydrolysis Tests & Results (Runs 6, 7, & 8).

The objective of these tests is to clearly determine and define the optimum operating parameters for the Composition B and Composition B4 explosives hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Blue Grass Chemical Agent Disposal Facility for the destruction of the explosives contained in the 8-inch Projectile, Chemical Agent GB, M42; 155mm Rocket, Chemical Agent GB, M55; 155mm Projectile, Chemical Agent VX, M121/A1; 155mm Rocket, Chemical Agent VX, M55 and 155mm Rocket Warhead, Chemical Agent VX, M56.

The table below identifies the process operating parameters for Runs 6, 7, and 8.

Table 6-1. Composition B4 Explosive Test Parameters

Operating Condition	Run 6	Run 7	Run 8
Composition B4 Feed Rate, lbs/hr			
1 <sup>st</sup> hour	50	50	50
2 <sup>nd</sup> hour	100	100	100
3 <sup>rd</sup> hour	150	150	150
4th hour	200	200	200
Caustic Soda Concentration, wt%	12	18	25
Caustic Soda Feed, gal	700	700	700
Reactor Operating Temperature, °C	87	87	87
Agitation Speed, RPM	70	70	70
Date Conducted	2/15/2001	2/20/2001	2/26/2001

The following charts present the process operating and control parameters for hydrolysis of Composition B4 explosive for Runs 6 and 8. The chart for Run 7 is not included because the data logger failed to record the proper time sequence.

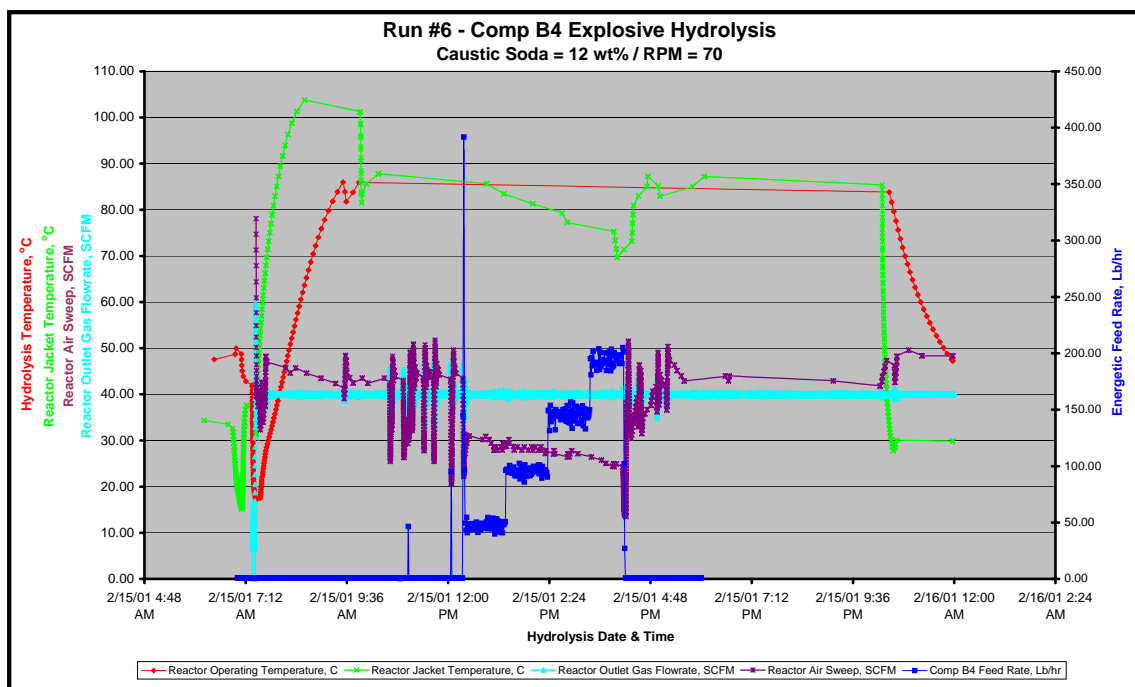


Figure 6-1. Run 6, Process Operating and Control Parameters

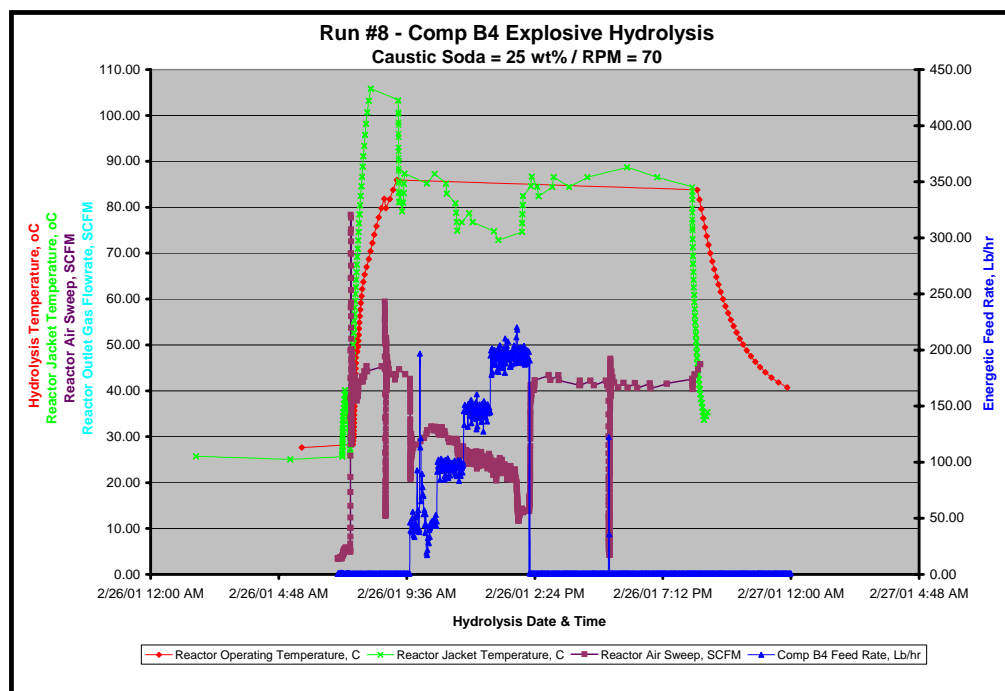


Figure 6-2. Run 8, Process Operating and Control Parameters

#### 6.1.1 Tests Results:

The plots present Composition B4 explosive destruction as a function of reactor residence time.

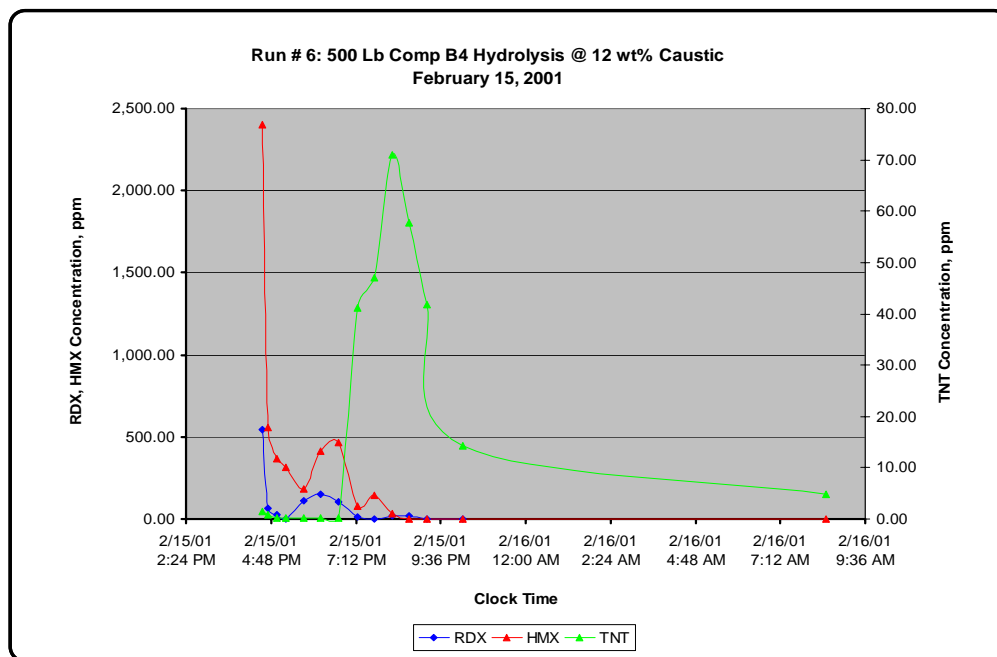


Figure 6-3. Run 6, Mid-Run Destruction Efficiency

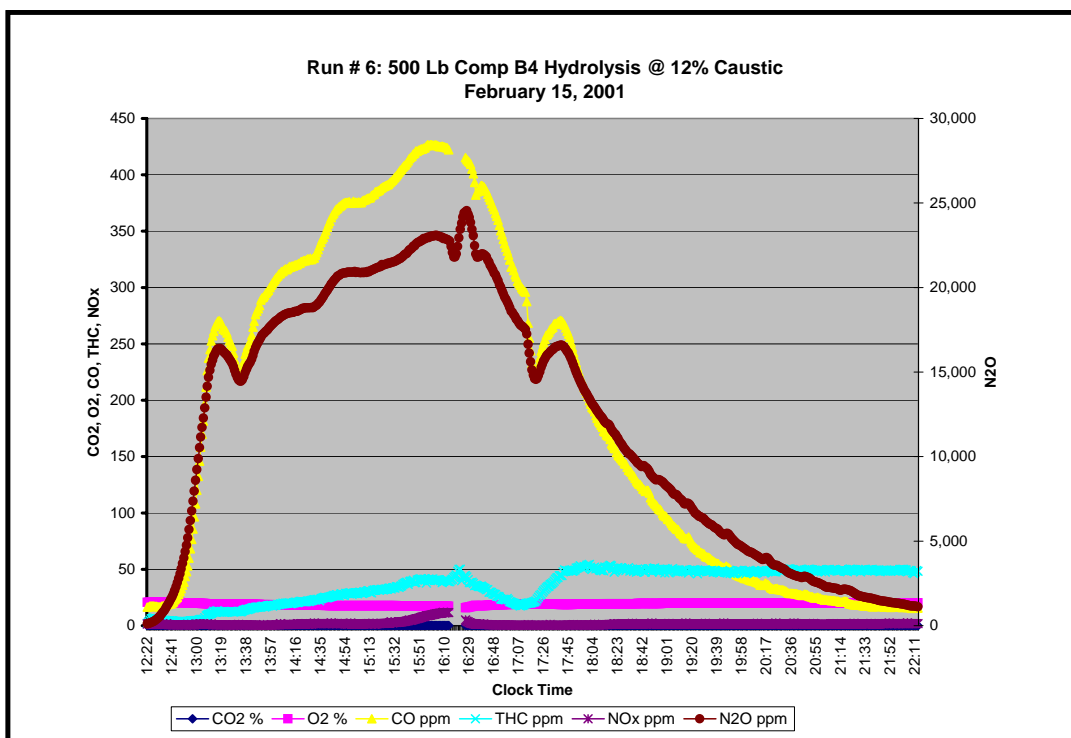


Figure 6-4. Run 6, Off-gas Production

Table 6-2. Run 6, Composition B4 End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	1,700.00	mg/l	1,700.00	
Aluminum	3,620.00	ug/l	3.62	
Ammonia	1,720.00	mg/l	1,720.00	
Calcium	90,300.00	ug/l	90.30	
Chloride	370.00	mg/l	370.00	J
Chromium	120.00	ug/l	0.12	J
Cobalt	100.00	ug/l	0.10	J
Copper	1,300.00	ug/l	1.30	
Cyanide (Sodium Cyanide)	39,200.00	ug/l	39.20	
Formate	10,900.00	mg/l	10,900.00	
Iron	3,700.00	ug/l	3.70	J
Lead	380.00	ug/l	0.38	J
Magnesium	7,120.00	ug/l	7.12	
Mercury	1.20	ug/l	0.00	J
Nitrite-N	3,800.00	mg/l	3,800.00	
Sodium	53,300,000.00	ug/l	53,300.00	
Sulfate	92.00	mg/l	92.00	J
TNT	4,890.00	ug/l	4.89	
Zinc	6,830.00	ug/l	6.83	
TIC	983.50	mg/l	983.50	
TOC	13,053.33	mg/l	13,053.33	
COD	30,800.00	mg/l	30,800.00	
Total Dissolved Solids	141,000.00	mg/l	141,000.00	
Total Suspended Solids	308.00	mg/l	308.00	
Normality as NaOH	1.64	n		
Density	1.09	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-3. Run 6, Composition B4 Off-gas Analysis

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	28.60	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	6.29	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	6,940.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	165.00	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	37.20	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	34.40	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	51.60	MAX			ug/m <sup>3</sup>
Acetaldehyde	1,060.00		41.50		ug/m <sup>3</sup>
Acetone	555.00		103.00		ppbv
Acetonitrile	1,952.16	J			ppbv
Ammonia	5,030,000.00		16,900,000.00		ug/m <sup>3</sup>
Benzene	17.70				ppbv
Bromodichloromethane	26.80				ppbv
Bromoform	16.50				ppbv
Butanal	36.00		13.00		ug/m <sup>3</sup>
Carbon Dioxide	0.08		0.05		%
Carbon Monoxide	284.00		112.00		ppmv
Chloroform	15.30				ppbv
Crotonaldehyde	9.71		2.37	J	ug/m <sup>3</sup>
Cyanide	0.01		0.01		ug/m <sup>3</sup>
Cyclohexanone			396.00		ug/m <sup>3</sup>
Decanal	1,170.00		91.00		ug/m <sup>3</sup>
Dibromochloromethane	35.60				ppbv
Formaldehyde			807.00		ug/m <sup>3</sup>
Heptanal	71.70		23.30		ug/m <sup>3</sup>
Hexanal	279.00		4.98	J	ug/m <sup>3</sup>
HMX	10.00	MAX			ug/m <sup>3</sup>
Isopropyl Alcohol			260.82	J	ppbv
m-Tolualdehyde	99.10		10.40		ug/m <sup>3</sup>
Nitrous Oxide	16,394.00		9,231.00		ppmv
Nonanal	60.10				ug/m <sup>3</sup>
NOx	0.90		0.00		ppmv
Octanal	63.50		23.40		ug/m <sup>3</sup>
Oxygen	19.00		20.20		%
Pentanal	6.30	J			ug/m <sup>3</sup>
Propanal	533.00		21.30		ug/m <sup>3</sup>
RDX	264.00	MAX			ug/m <sup>3</sup>
Total Hydrocarbons	27.60		70.80		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

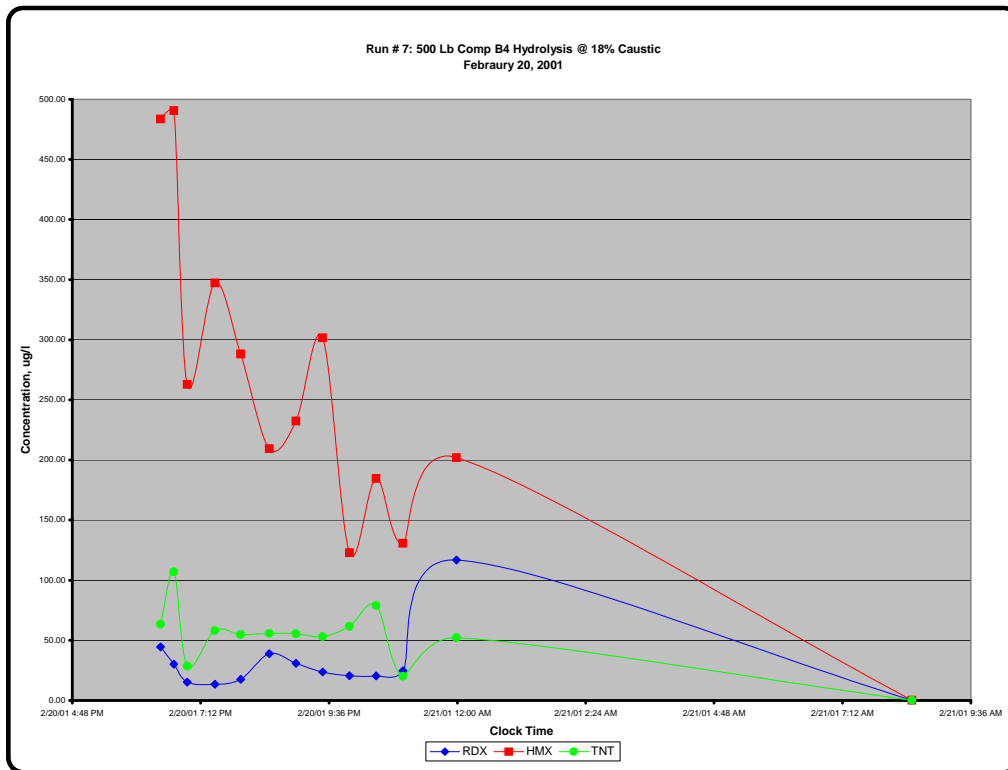


Figure 6-5. Run 7, Mid-Run Destruction Efficiency

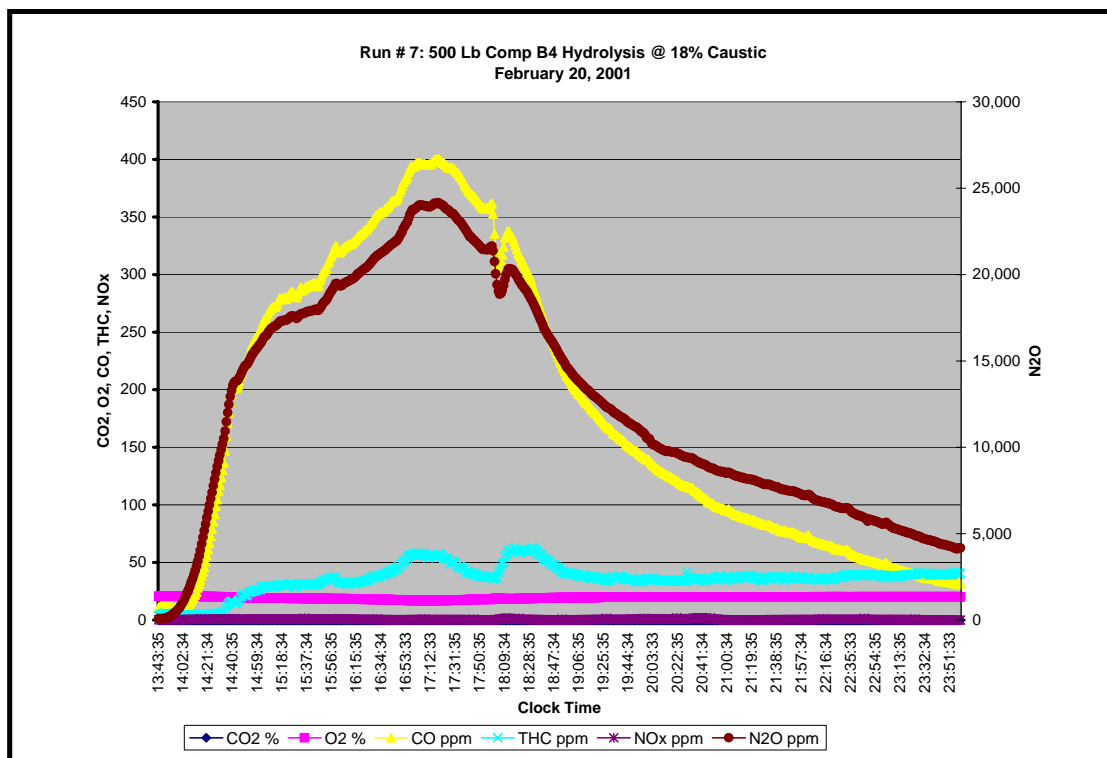


Figure 6-6. Run 7, Off-gas Production

Table 6-4. Run 7, Composition B4 End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	2,120.00	mg/l	2,120.00	
Aluminum	3,400.00	ug/l	3.40	
Ammonia	1,760.00	mg/l	1,760.00	
Calcium	70,600.00	ug/l	70.60	
Chloride	390.00	mg/l	390.00	J
Chromium	140.00	ug/l	0.14	J
Cobalt	110.00	ug/l	0.11	J
Copper	1,670.00	ug/l	1.67	
Cyanide (Sodium Cyanide)	59,200.00	ug/l	59.20	
Fluoride	96.00	mg/l	96.00	J
Formate	16,200.00	mg/l	16,200.00	
Iron	5,100.00	ug/l	5.10	J
Lead	330.00	ug/l	0.33	J
Magnesium	2,430.00	ug/l	2.43	
Molybdenum	110.00	ug/l	0.11	J
Nitrite-N	4,300.00	mg/l	4,300.00	
Potassium	84,000.00	ug/l	84.00	J
Sodium	84,800,000.00	ug/l	84,800.00	
TNT	4,890.00	ug/l	4.89	
Zinc	1,250.00	ug/l	1.25	
TIC	1,090.00	mg/l	1,090.00	
TOC	16,960.00	mg/l	16,960.00	
COD	34,300.00	mg/l	34,300.00	
Total Dissolved Solids	214,000.00	mg/l	214,000.00	
Total Suspended Solids	500.00	mg/l	500.00	
Normality as NaOH	3.00	n		
Density	1.17	g/ml		

J = Estimated Value; concentration is below limit of quantification



Table 6-5. Run 7, Composition B4 Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	21.90	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	6.89	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	7,170.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	195.00	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	113.00	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	32.80	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	65.30	MAX			ug/m <sup>3</sup>
Acetaldehyde	1,170.00		91.00		ug/m <sup>3</sup>
Acetone	322.00		206.00		ppbv
Acetonitrile	2,288.48	J	662.45	J	ppbv
Ammonia	10,300,000.00		23,300,000.00		ug/m <sup>3</sup>
Bromodichloromethane	26.80		5.40	U	ppbv
Butanal	42.90		33.00		ug/m <sup>3</sup>
Carbon Dioxide	0.04		0.02		%
Carbon Monoxide	260.00		109.00		ppmv
Chloroform	49.80		5.40	U	ppbv
Crotonaldehyde	9.74		5.03	J	ug/m <sup>3</sup>
Cyanide	0.02		0.01		ug/m <sup>3</sup>
Cyclohexanol	48.55	J			ppbv
Cyclohexanone	14,300.00	D	540.00		ug/m <sup>3</sup>
Decanal	1,770.00		161.00		ug/m <sup>3</sup>
Dibromochloromethane	12.40		5.40	U	ppbv
Ethanol			36.00	J	
Formaldehyde	10,300.00	D	1,470.00		ug/m <sup>3</sup>
Heptanal	53.50		30.30		ug/m <sup>3</sup>
Hexanal	92.60		39.80	J	ug/m <sup>3</sup>
HMX	7.99	MAX			ug/m <sup>3</sup>
Isopropyl Alcohol	262.82	J		J	ppbv
m-Tolualdehyde	88.40		28.10		ug/m <sup>3</sup>
Nitrous Oxide	16,481.00		9,856.00		ppmv
Nonanal	54.60		28.80		ug/m <sup>3</sup>
NOx	0.50		0.50		ppmv
Octanal	59.30		27.90		ug/m <sup>3</sup>
Oxygen	19.20		20.30		%
Pentanal	4.88	J	0.43	U	ug/m <sup>3</sup>
Propanal	439.00		48.50		ug/m <sup>3</sup>
RDX	174.00	MAX			ug/m <sup>3</sup>
Toluene	2.14		5.40	U	ppbv
Total Hydrocarbons	43.60		50.50		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

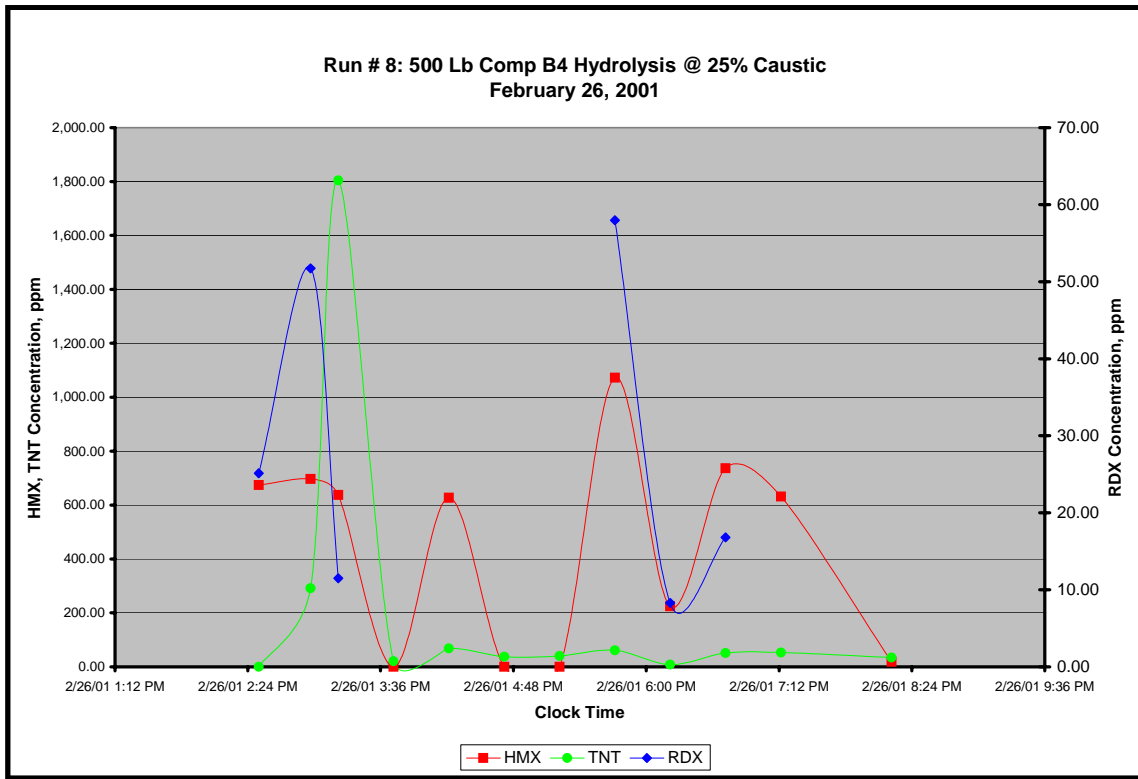


Figure 6-7. Run 8, Mid-Run Destruction Efficiency

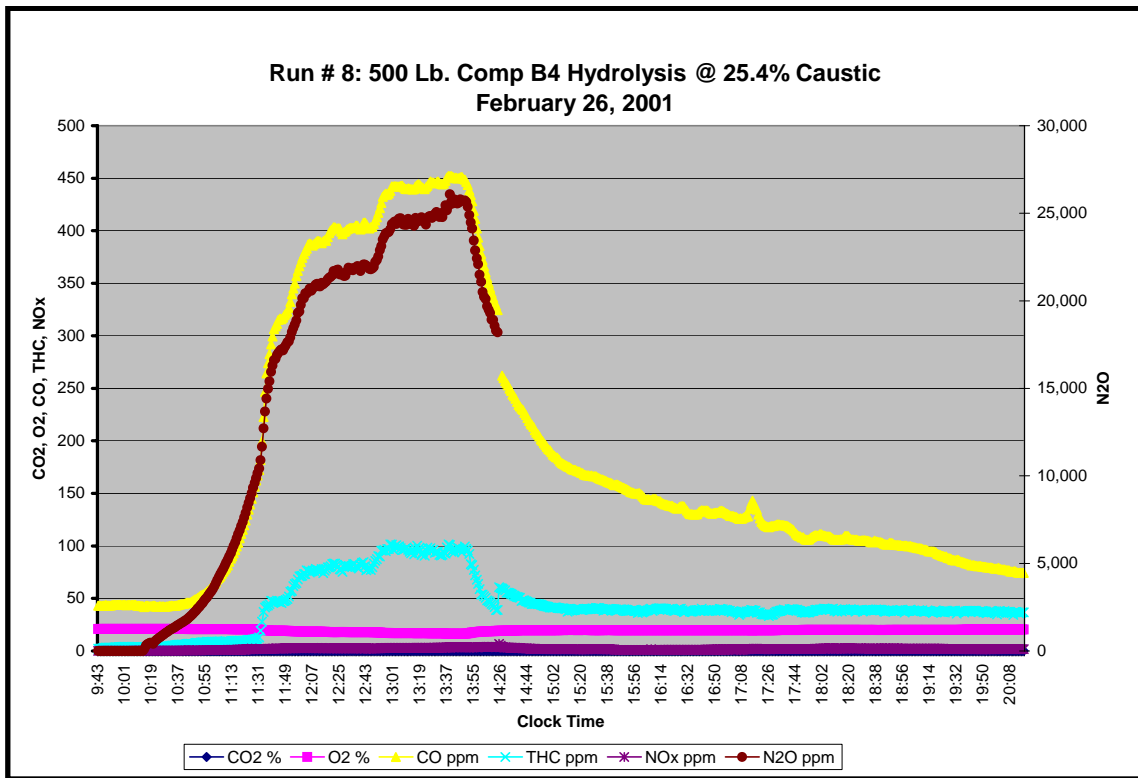


Figure 6-8. Run 8, Off-gas Production

Table 6-6. Run 8, Composition B4 End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	1,110.00	mg/l	1,110.00	
Aluminum	3,770.00	ug/l	3.77	
Ammonia	1,320.00	mg/l	1,320.00	
Beryllium	2.60	ug/l	0.0026	J
Calcium	72,600.00	ug/l	72.6	
Chromium	310.00	ug/l	0.31	J
Cobalt	120.00	ug/l	0.12	J
Copper	1,840.00	ug/l	1.84	
Cyanide (Sodium Cyanide)	136,000.00	ug/l	136	
Fluoride	98.00	mg/l	98.00	J
Formate	12,100.00	mg/l	12,100.00	
Iron	5,900.00	ug/l	5.9	J
Lead	370.00	ug/l	0.37	J
Magnesium	6,660.00	ug/l	6.66	
Manganese	62.00	ug/l	0.062	J
Molybdenum	160.00	ug/l	0.16	J
Nickel	600.00	ug/l	0.6	J
Nitrate-N	10.00	mg/l	10.00	J
Nitrite-N	4,200.00	mg/l	4,200.00	
Potassium	128,000.00	ug/l	128	
Sodium	124,000,000.00	ug/l	124000	
Sulfate	190.00	mg/l	190.00	
Zinc	28,000.00	ug/l	28	
TIC	1,018.50	mg/l	1,018.50	
TOC	3.48	mg/l	3.48	
COD	29,400.00	mg/l	29,400.00	
Total Suspended Solids	817.00	mg/l	817.00	
Total Dissolved Solids	292,000.00	mg/l	292,000.00	
Normality as NaOH	5.15	n		
Density	1.22	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-7. Run 8, Composition B4 Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	7.10	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	15.90	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	53.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	9,870.00	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	1.51	MAX			ug/m <sup>3</sup>
Acetaldehyde	1,820.00	D	216.00		ug/m <sup>3</sup>
Acetone	436.00		4.40	U	ppbv
Ammonia	18,300,000.00		12,900,000.00		ug/m <sup>3</sup>
Bromodichloromethane	13.40		4.40	U	ppbv
Butanal	62.40		21.00		ug/m <sup>3</sup>
Carbon Dioxide	0.03		0.04		%
Carbon Monoxide	229.00		91.00		ppmv
Chloroform	25.60		4.40	U	ppbv
Crotonaldehyde	0.37	U	6.08		ug/m <sup>3</sup>
Cyanide	0.02		0.01		ug/m <sup>3</sup>
Cyclohexane	394.23	J			ppbv
Cyclohexanone	31,200.00	D	859.00		ug/m <sup>3</sup>
Decanal	6,770.00	D	151.00		ug/m <sup>3</sup>
Formaldehyde	13,100.00	D	1,730.00	B	ug/m <sup>3</sup>
Heptanal	34.50		22.00		ug/m <sup>3</sup>
Hexanal	426.00		63.60		ug/m <sup>3</sup>
Methyl Chloride	186.00	B	143.00	B	ppbv
m-Tolualdehyde	65.30		17.40		ug/m <sup>3</sup>
Nitrous Oxide	14,417.00				ppmv
Nonanal	44.40		1.44	U	ug/m <sup>3</sup>
NOx	2.10		2.00		ppmv
Octanal	46.70		0.58	U	ug/m <sup>3</sup>
Oxygen	19.30		20.10		%
RDX	4.01	MAX			ug/m <sup>3</sup>
Toluene	14.00		4.40	U	ppbv
Total Hydrocarbons	47.10		38.00		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

### 6.1.2 Discussion & Analysis:

1. The end of run liquid analyses indicates that the destruction rate efficiency achieved approximately 5 hours after cessation of the feeding of Composition B4 explosive to the reactor – 9 hours after the start of the run ranged from 99.9884% to 100.00%. 100% of the HMX and RDX was destroyed, while the TNT destruction rate efficiency ranged from 99.9711 to 100.00%
2. The variability in the energetics concentration in the mid run samples for the Composition B4 runs is most likely due to the fact that some energetic particles are entering and passing through the recycle loop where the samples are being collected by the auto-sampler system.
3. The only “bad actor” detected in the hydrolysate is cyanide (possibly sodium cyanide) at a range of 39 to 139 ppm, increasing in concentration with increasing caustic strength. However, previous work performed under the AWCA program had reported that the hydrolysis of energetics produced cyanide and that the subsequent treatment of said hydrolysate using SCOW technology adequately reduces the hazardous compound concentrations in the hydrolysate feeds; i.e., cyanide was reduced to less than 36 mg/L, well below levels of concern. (PM ACWA, 1999 Supplemental Report to Congress, p. B.4-64 and PM ACWA, 2001 Supplement report to Congress, p C.4-44)) Therefore, at the levels present, no problems are anticipated completing the processing of the hydrolysate using the SCWO system or bioreactor systems.
4. The energetics loading for the three runs with Composition B4 is 6-7 weight-percent resulting in a total solids (dissolved and suspended) loading at the end of the run of between 14-to-29 weight-percent depending on the caustic strength.
5. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. The off gassing (see Figures 6-4, 6-6 and 6-8) tracks nicely with the addition of the Composition B4 explosive and fell off very quickly after the addition was completed, indicating that the most of the reactions are taking place during energetic addition and progressing to completion in line with the liquid analysis data.
6. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
7. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. At this level, foaming was not a problem since the agitator formed a clearly defined vortex that quickly dispersed the foam back into the solution. The agitator speed was controlled at approximately 70 rpm throughout the test.
8. Examination of the off-gas characterization for the three runs indicates that some energetic materials (1,3,5-Trinitrobenzene, Dinitrotoluene, TNT, RDX, HMX) at low levels were entrained in the gas stream during the addition phase of the process. TNT has a measurable vapor pressure at ambient, therefore one would expect TNT to come-off as part of the off-gassing stream. The presence of RDX and HMX in of the off-gas stream is most likely attributed to these materials becoming entrained in water droplets and evolved with the off gas. Also, some dusting occurs as the Composition B4 falls into the reactor through the headspace air stream, possibly contributing to these readings. The energetic materials disappeared from the air stream once the additional was stopped. Use of a condenser, just above the reactor, to drop any entrained materials back into the reactor should be effective.

9. The only significant “bad actors” identified in the off-gas characterization were cyanide, toluene and benzene; however the levels were extremely low and the subsequent SCOW process will complete the destruction of these compounds.
10. The major constituents of the off gassing were ammonia, nitrous oxide, cyclohexanone and formaldehyde. These gasses can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release. The average range concentration of CO<sub>2</sub>, O<sub>2</sub>, CO, THC, NO<sub>x</sub> and N<sub>2</sub>O in the off gas stream during energetic addition for the three runs was: 0.03 - .08%, 19.0 – 19.3%, 229 – 284 ppmvd, 27.6 – 47.1 ppmvd, 0.5 – 2.1 ppmvd, 14,005 – 16,481 ppmvd, respectively and during digestion the concentration was: 0.02 - 0.05%, 20.1 – 20.3%, 91 – 112 ppmvd, 38 – 70.8 ppmvd, 0.0 – 2 ppmvd, 9,231 – 9,856 ppmvd, respectively.
11. The inorganic materials (metals) detected in the hydrolysate end of runs analysis are sourced from the sodium hydroxide stock feed that contains some of these components.

## 6.2 M1 Propellant Hydrolysis Tests & Results (Runs 9, 10, 11 and 14).

The objective of these tests is to clearly determine and define the optimum operating parameters for the M1 propellant hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Pueblo Chemical Agent Disposal Facility for the destruction of propellants contained in the 105mm Projectile, Chemical Agent HD, M60.

The table below identifies the process operating parameters for Runs 9, 10, 11, and 14.

Table 6-8. M1 Propellant Test Parameters

Operating Condition	Run 9	Run 10	Run 11	Run 14 Extended
M1 Feed Rate, lbs/hr				
1 <sup>st</sup> hour	50	50	50	50
2 <sup>nd</sup> hour	100	100	100	100
3 <sup>rd</sup> hour	150	150	150	150
4th hour	200	200	200	200
Caustic Soda Concentration, wt%	11.3	20	25	20
Caustic Soda Feed, gal	700	700	700	700
Reactor Operating Temperature, °C	87	87	87	87
Agitation Speed, RPM	70	70	70	70
Date Conducted	2/28/2001	3/2/2001	3/7/2001	3/15/2001

Run 14 was conducted over a 24-hour period to determine if the off gassing would finally cease and an endpoint reached. Off gassing was still taking place after 24-hours had elapsed.

The following charts present the process operating and control parameters for hydrolysis of M1 propellant:

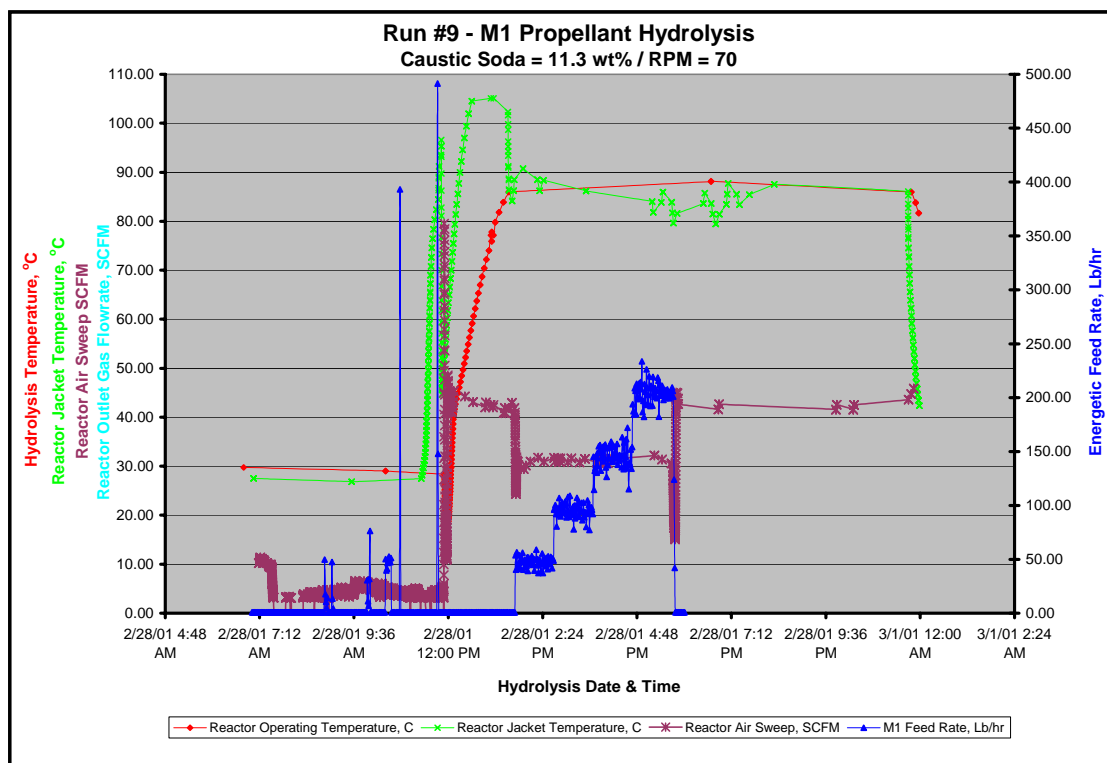


Figure 6-9. Run 9, Process Operating and Control Parameters

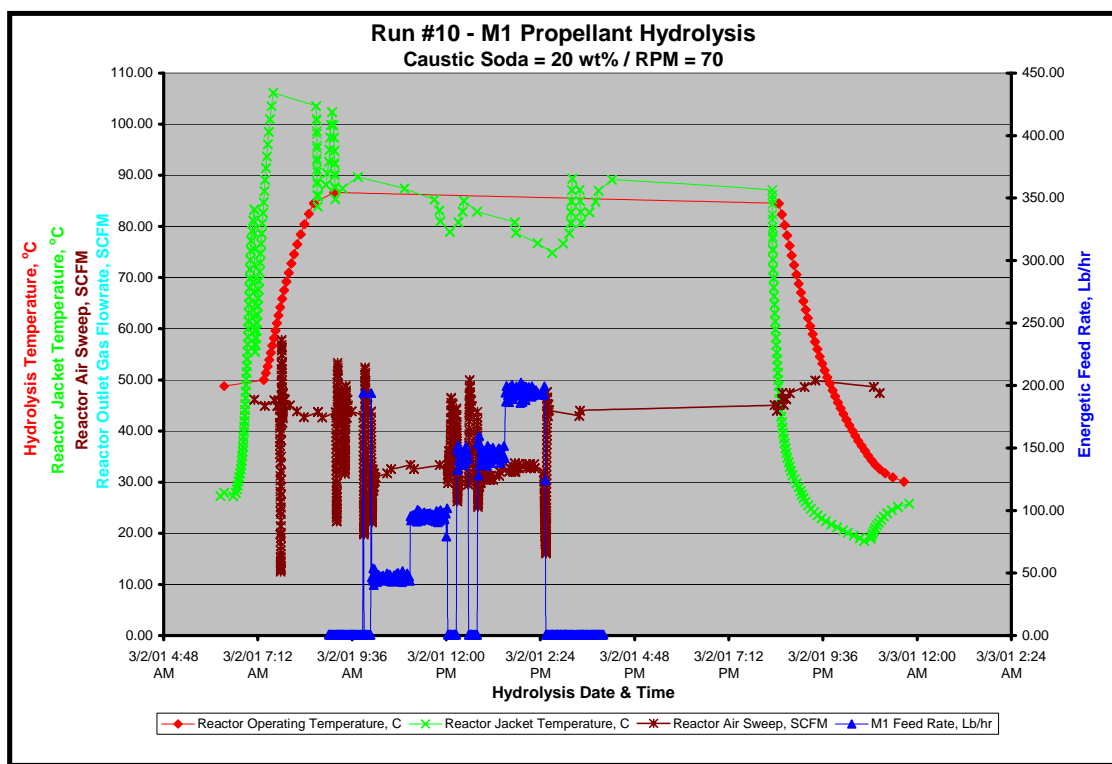


Figure 6-10. Run 10, Process Operating and Control Parameters

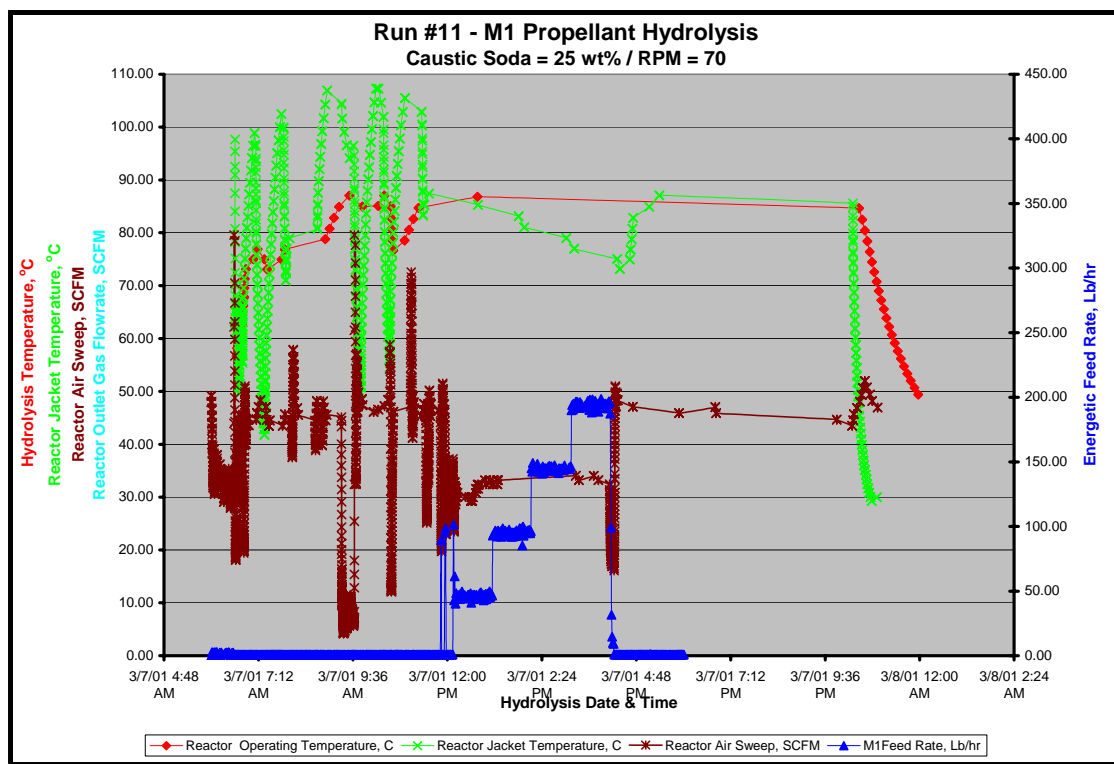


Figure 6-11. Run 11, Process Operating and Control Parameters



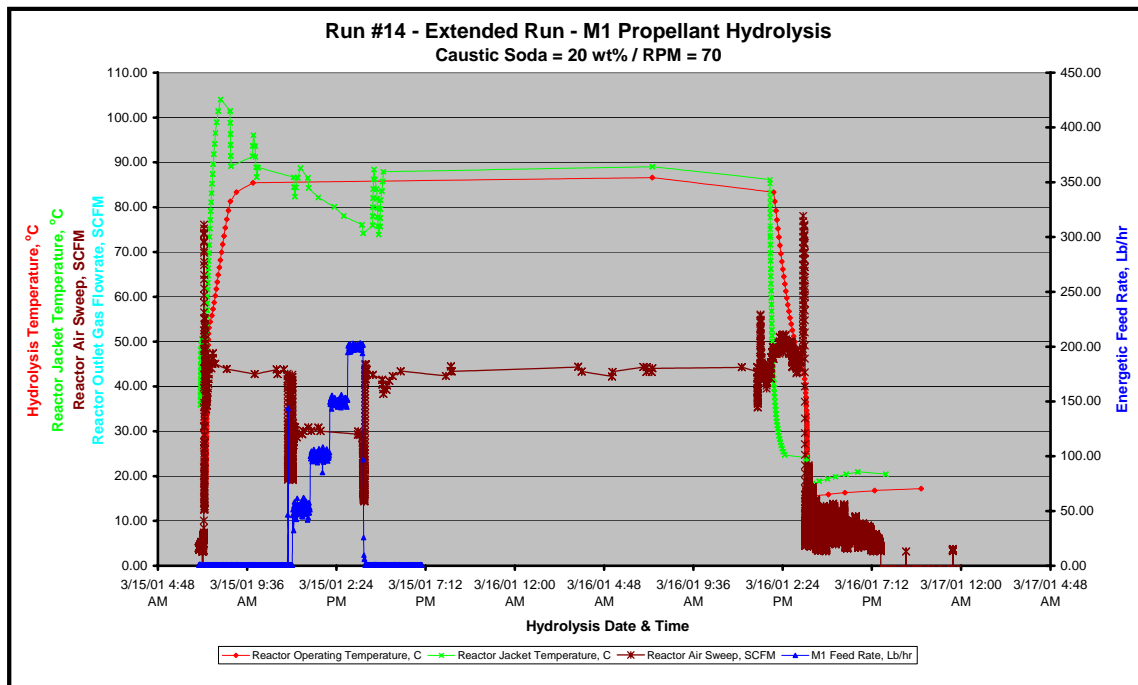


Figure 6-12. Run 14, Process Operating and Control Parameters (Extended Run)

#### 6.2.1 Tests Results:

The plots below represent M1 propellant destruction as a function of reactor residence time. Run 14, the extended run was conducted to determine at what time the total hydrocarbon in the off gas stream would start to level off and decrease.

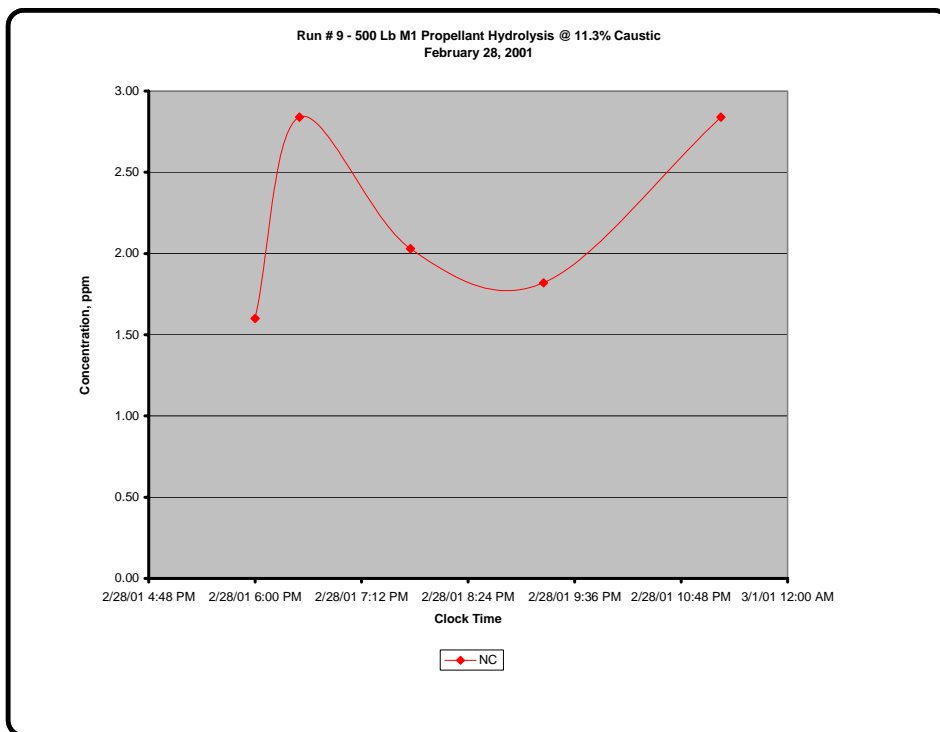


Figure 6-13. Run 9, Mid-Run Destruction Efficiency

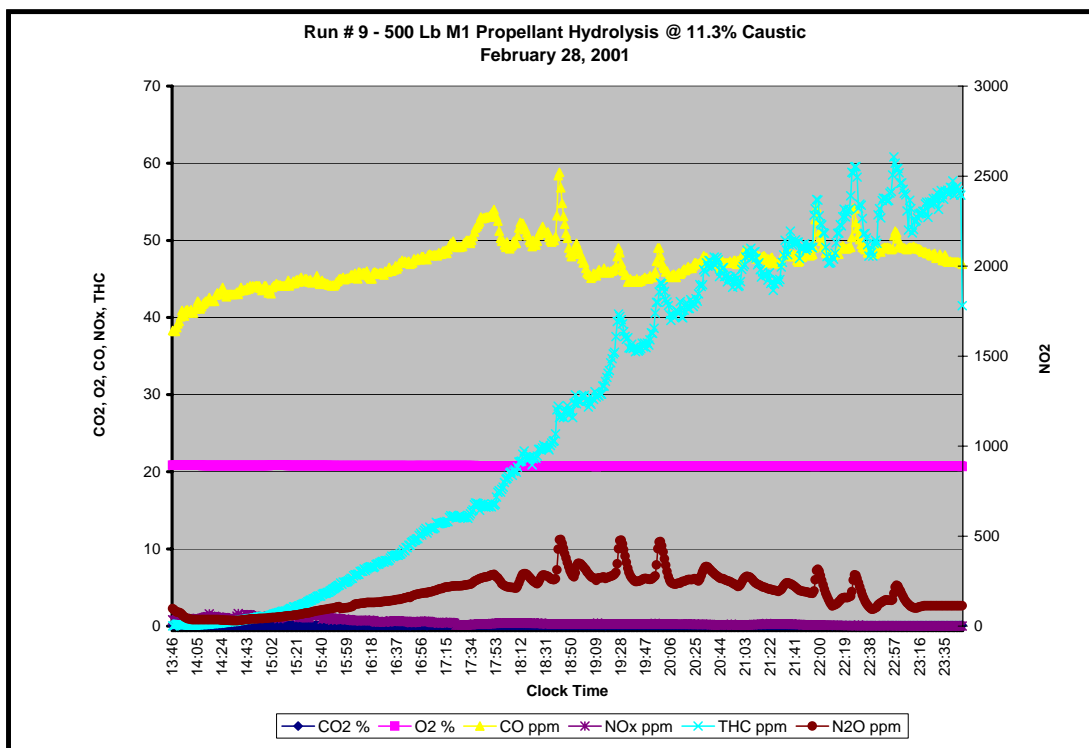


Figure 6-14. Run 9, Off-gas Production

Table 6-9. Run 9, M1 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
2,4-Dinitrotoluene	740.00	ug/l	0.74	J
2-Methylphenol	640.00	ug/l	0.64	J
4-Nitrophenol	1,600.00	ug/l	1.60	J
Acetate	5,120.00	mg/l	5,120.00	
Ammonia	54.00	mg/l	54.00	
Barium	97.50	ug/l	0.10	
bis(2-Ethylhexyl)phthalate	400.00	ug/l	0.40	J
Calcium	40,600.00	ug/l	40.60	
Chloride	40.00	mg/l	40.00	J
Chromium	109.00	ug/l	0.11	
Copper	1,120.00	ug/l	1.12	
Cyanide (Sodium Cyanide)	29,400.00	ug/l	29.40	
Fluoride	589.00	mg/l	589.00	
Formate	1,290.00	mg/l	1,290.00	
Iron	4,000.00	ug/l	4.00	
Magnesium	9,150.00	ug/l	9.15	
Manganese	34.30	ug/l	0.03	
Nickel	104.00	ug/l	0.10	
Nitrate-N	1,480.00	mg/l	1,480.00	
Nitrite-N	4,180.00	mg/l	4,180.00	
Nitrobenzene	260.00	ug/l	0.26	J
Potassium	11,600.00	ug/l	11.60	
Sodium	45,900,000.00	ug/l	45,900.00	
Sulfate	138.00	mg/l	138.00	
Zinc	269.00	ug/l	0.27	
TIC	765.00	mg/l	765.00	
TOC	14,475.00	mg/l	14,475.00	
COD	40,700.00	mg/l	40,700.00	
Total Suspended Solids	640.00	mg/l	640.00	
Total Dissolved Solids	126,000.00	mg/l	126,000.00	
Normality as NaOH	1.30	n		
Density	1.09	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-10. Run 9, M1 Propellant Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
2-Butanone	570.00	U	1,040.00		ppbv
Acetaldehyde	15,200.00	D	15,700.00	D	ug/m <sup>3</sup>
Acetone	29,900.00		78,200.00		ppbv
Ammonia	198,000.00		618,000.00		ug/m <sup>3</sup>
Benzene	15.00	U	43.20		ppbv
Bromodichloromethane	26.40		14.00	U	ppbv
Butanal	92.80		389.00		ug/m <sup>3</sup>
Carbon Dioxide	0.04		0.04		%
Carbon Monoxide	2.00		5.00		ppmv
Chloroform	24.20		14.00	U	ppbv
Cyanide	0.01	U	0.02		mg/m <sup>3</sup>
Cyclohexane	133,053.00	J	248,135.40	J	ppbv
Cyclohexanone	1,110.00		120.00		ug/m <sup>3</sup>
Decanal	162.00		22.90		ug/m <sup>3</sup>
Dibromochloromethane	21.90		14.00	U	ppbv
Ethyl ether	17,673.00	J	36,905.00	J	ppbv
Formaldehyde	688.00	B	251.00	B	ug/m <sup>3</sup>
Heptanal	252.00		53.30		ug/m <sup>3</sup>
Hexanal	165.00		44.20		ug/m <sup>3</sup>
Methyl Chloride	31.60	B	26.40	B	ppbv
m-Tolualdehyde	48.10		40.10		ug/m <sup>3</sup>
Nitrous Oxide	113.00		232.00		ppmv
Nonanal	22.70		15.20		ug/m <sup>3</sup>
NOx	0.70		0.00		ppmv
Octanal	0.46	U	14.10		ug/m <sup>3</sup>
Oxygen	21.30		21.20		%
Pentanal	27.50		26.40		ug/m <sup>3</sup>
Toluene	12,100.00		42,200.00		ppbv
Xylenes	22.50	U	34.70		ppbv
Total Hydrocarbons	240.30		1,680.70		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

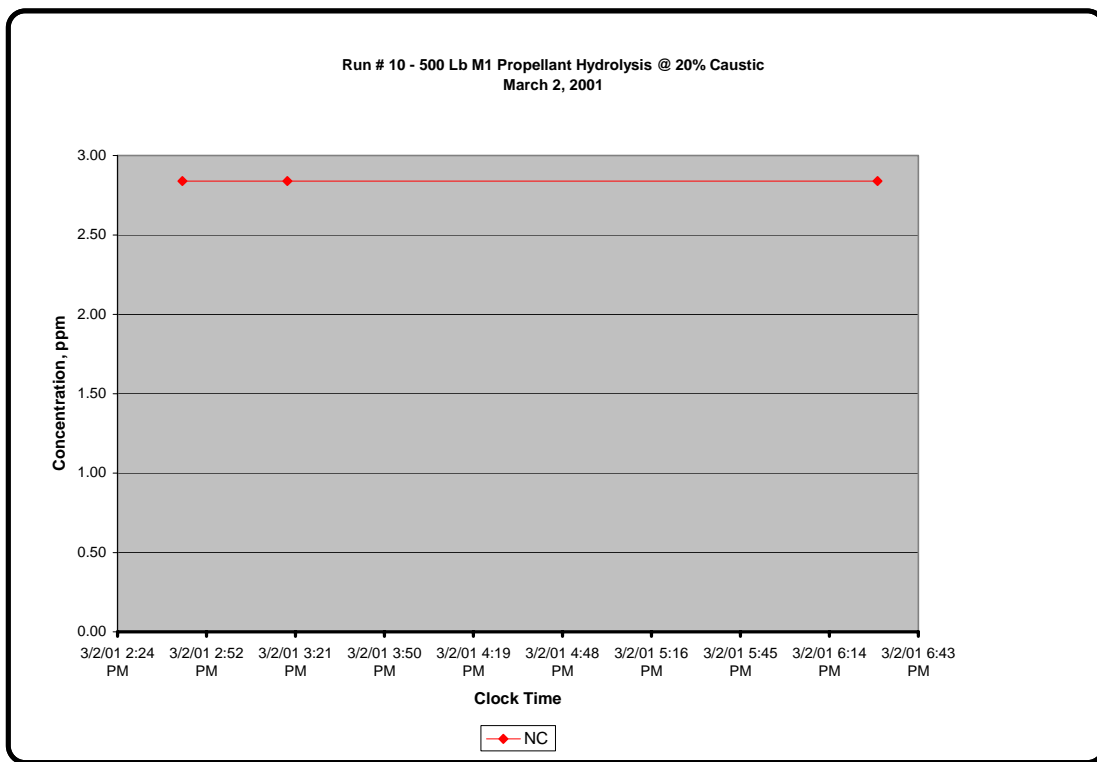


Figure 6-15. Run 10, Mid-Run Destruction Efficiency

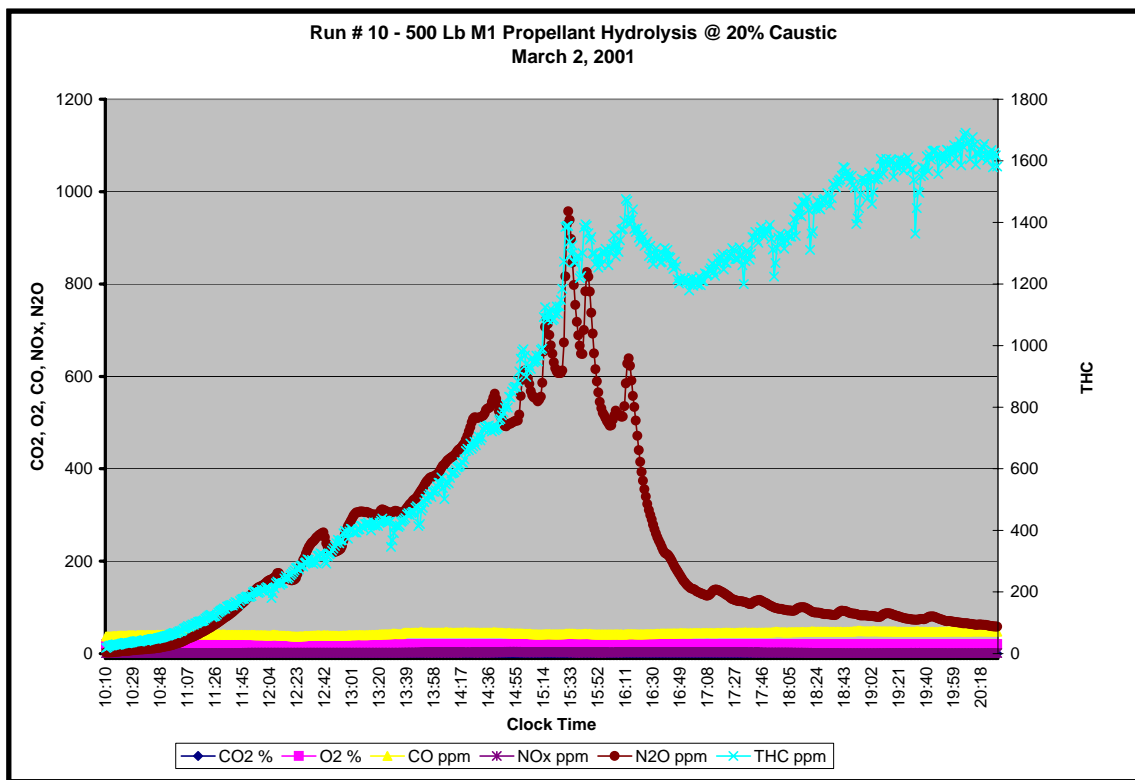


Figure 6-16. Run 10, Off-gas Production

Table 6-11. Run 10, M1 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
2-Methylphenol	5,600.00	ug/l	5.60	J
4-Nitrophenol	3,000.00	ug/l	3.00	
Acetate	6,130.00	mg/l	6,130.00	
Aluminum	393.00	ug/l	0.39	
Ammonia	55.50	mg/l	55.50	J
Barium	174.00	ug/l	0.17	
Calcium	34,500.00	ug/l	34.50	
Chromium	176.00	ug/l	0.18	
Cobalt	104.00	ug/l	0.10	J
Copper	941.00	ug/l	0.94	
Cyanide (Sodium Cyanide)	76,000.00	ug/l	76.00	
Di-n-octylphthalate	3,000.00	ug/l	3.00	
Fluoride	851.00	mg/l	851.00	J
Formate	1,740.00	mg/l	1,740.00	
Iron	6,170.00	ug/l	6.17	
Magnesium	7,490.00	ug/l	7.49	
Manganese	45.90	ug/l	0.05	J
Molybdenum	28.80	ug/l	0.03	
Nickel	176.00	ug/l	0.18	
Nitrate-N	1,780.00	mg/l	1,780.00	
Nitrite-N	5,060.00	mg/l	5,060.00	J
o-Phosphate-P	526.00	mg/l	526.00	
Phosphorus	122.00	ug/l	0.12	
Potassium	43,900.00	ug/l	43.90	
Sodium	92,840,000.00	ug/l	92,840.00	J
Sulfate	196.00	mg/l	196.00	
Zinc	435.00	ug/l	0.44	
TIC	1,121.75	mg/l	1,121.75	
TOC	17,825.00	mg/l	17,825.00	J
COD	19,600.00	mg/l	19,600.00	
Total Suspended Solids	1,280.00	mg/l	1,280.00	
Total Dissolved Solids	243,000.00	mg/l	243,000.00	
Normality as NaOH	3.75	n		
Density	1.18	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-12. Run 10, M1 Propellant Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	8.41	MAX			ug/m <sup>3</sup>
1-Butanol	161,586.80	J			ppbv
2,4,6-Trinitrotoluene	119.00	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	716.00				ug/m <sup>3</sup>
2,6-Dinitrotoluene	3.37	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	3.13	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	3.34	MAX			ug/m <sup>3</sup>
Acetaldehyde	16,300.00	D	11,600.00	D	ug/m <sup>3</sup>
Acetone	37,800.00		89,000.00		ppbv
Ammonia	131,000.00		616,000.00		ug/m <sup>3</sup>
Butanal	123.00		807.00		ug/m <sup>3</sup>
Carbon Dioxide	0.03		0.03		%
Carbon Monoxide	0.00		3.00		ppmv
Crotonaldehyde	0.33	U	9.03		ug/m <sup>3</sup>
Cyanide	0.01	U	0.01		mg/m <sup>3</sup>
Cyclohexanone	49.10		68.10		ug/m <sup>3</sup>
Decanal	19.30		12.50		ug/m <sup>3</sup>
Ethyl ether	58,147.10	J	138,181.80	J	ppbv
Formaldehyde	300.00	B	128.00	B	ug/m <sup>3</sup>
Heptanal	23.60		24.40		ug/m <sup>3</sup>
Hexanal	124.00		64.30		ug/m <sup>3</sup>
HMX	4.31	MAX			ug/m <sup>3</sup>
Methyl Chloride	753.00	B	1,620.00	B	ppbv
m-Tolualdehyde	25.30		35.60		ug/m <sup>3</sup>
Nitrous Oxide	201.00		257.00		ppmv
Nonanal	16.80		13.90		ug/m <sup>3</sup>
NOx	0.60		1.00		ppmv
Octanal	15.80		12.90		ug/m <sup>3</sup>
Oxygen	21.30		21.30		%
Pentanal	35.60		15.30		ug/m <sup>3</sup>
RDX	9.77				ug/m <sup>3</sup>
Toluene	15,400.00		30,900.00		ppbv
Total Hydrocarbons	286.00		1,336.00		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

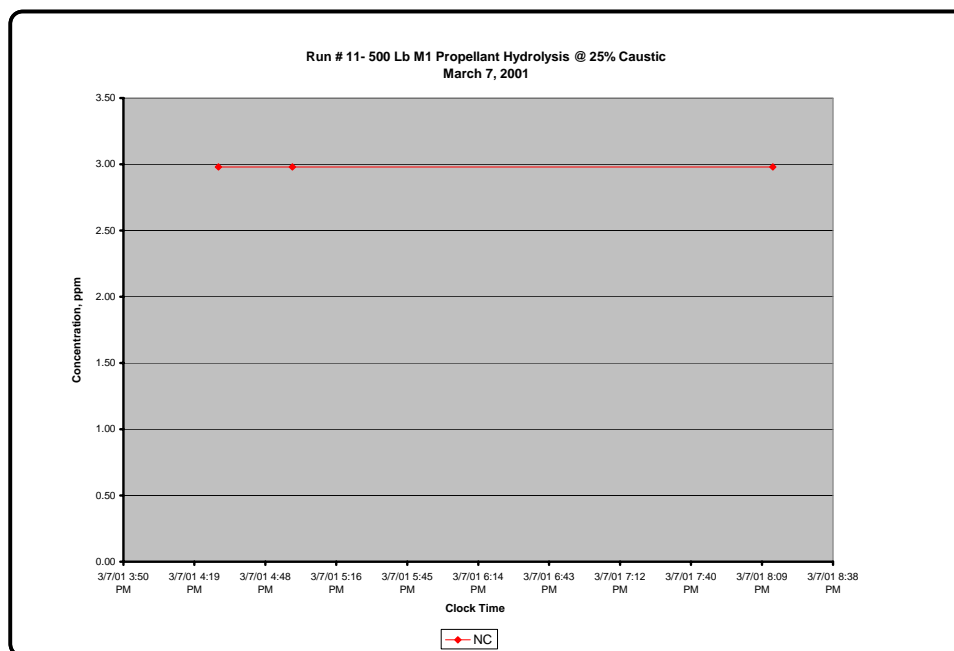


Figure 6-17. Run 11, Mid-Run Destruction Efficiency

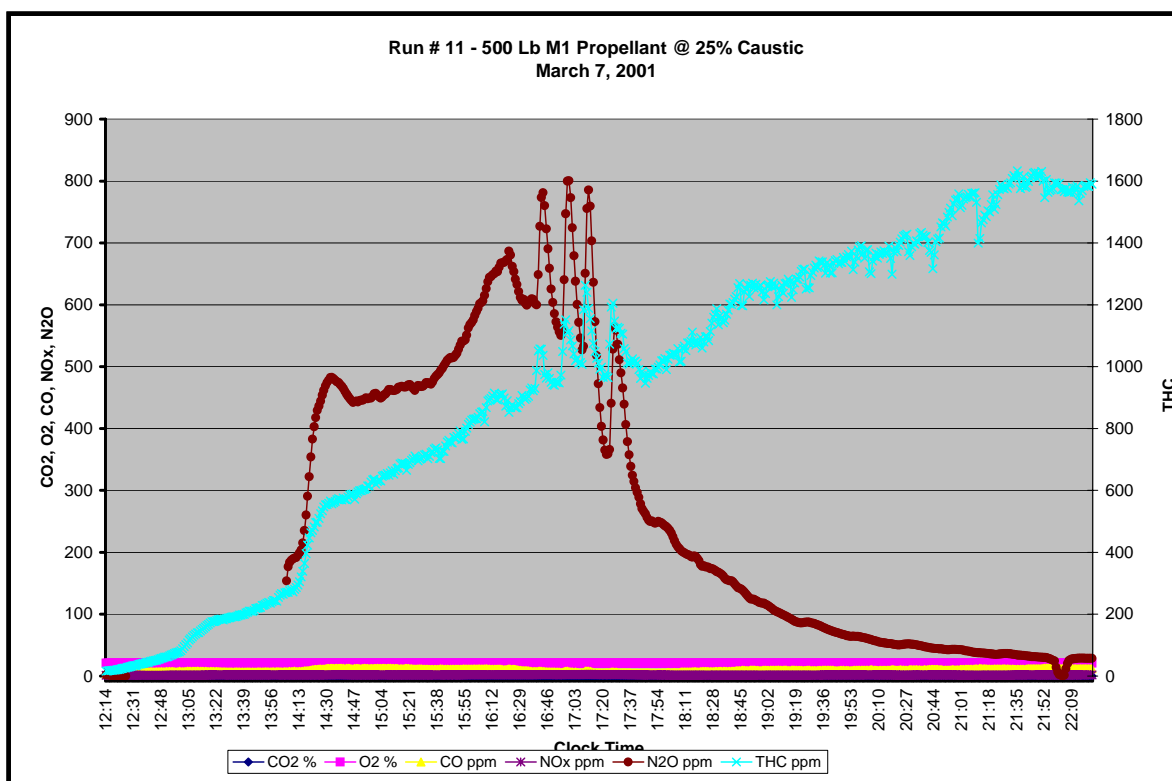


Figure 6-18. Run 11, Off-gas Production



Table 6-13. Run 11, M1 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
2-Methylphenol	1,400.00	ug/l	1.40	J
4-Nitrophenol	1,500.00	ug/l	1.50	J
Acetate	7,350.00	mg/l	7,350.00	
Aluminum	418.00	ug/l	0.42	
Ammonia	55.50	mg/l	55.50	
Barium	166.00	ug/l	0.17	
Calcium	30,000.00	ug/l	30.00	
Chloride	8,900.00	mg/l	8,900.00	
Chromium	221.00	ug/l	0.22	
Cobalt	101.00	ug/l	0.10	
Copper	843.00	ug/l	0.84	
Cyanide (Sodium Cyanide)	95,400.00	ug/l	95.40	
Fluoride	10,200.00	mg/l	10,200.00	
Formate	2,240.00	mg/l	2,240.00	
Iron	6,750.00	ug/l	6.75	
Magnesium	6,580.00	ug/l	6.58	
Manganese	59.20	ug/l	0.06	
Molybdenum	28.00	ug/l	0.03	J
Nickel	244.00	ug/l	0.24	
Nitrate-N	845.00	mg/l	845.00	
Nitrite-N	1,860.00	mg/l	1,860.00	
o-Phosphate-P	2,040.00	mg/l	2,040.00	
Phosphorus	498.00	ug/l	0.50	J
Potassium	57,200.00	ug/l	57.20	
Sodium	113,000,000.00	ug/l	113,000.00	
Sulfate	3,280.00	mg/l	3,280.00	
Zinc	442.00	ug/l	0.44	
TIC	1,167.50	mg/l	1,167.50	
TOC	16,825.00	mg/l	16,825.00	
COD	49,600.00	mg/l	49,600.00	
Total Suspended Solids	600.00	mg/l	600.00	
Total Dissolved Solids	295,000.00	mg/l	295,000.00	
Normality as NaOH	4.95	n		
Density	1.22	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-14. Run 11, M1 Propellant Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	2.21	MAX			ug/m <sup>3</sup>
1-Butanol	14,568.70	J	49,442.90	J	ppbv
2,4,6-Trinitrotoluene	43.90	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	21,600.00				ug/m <sup>3</sup>
2,6-Dinitrotoluene	2.97	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	1.63	MAX			ug/m <sup>3</sup>
Acetaldehyde	13,400.00	D	11,200.00	D	ug/m <sup>3</sup>
Acetone	44,800.00		50,800.00		ppbv
Ammonia	81,400.00		544,000.00		ug/m <sup>3</sup>
Butanal	203.00		1,000.00		ug/m <sup>3</sup>
Carbon Dioxide	0.03		0.04		%
Carbon Monoxide	2.00		1.00		ppmv
Crotonaldehyde	8.17		5.71		ug/m <sup>3</sup>
Cyanide	0.01	U	0.01		mg/m <sup>3</sup>
Cyclohexanone	22.70		79.10		ug/m <sup>3</sup>
Decanal	4.05	U	18.40		ug/m <sup>3</sup>
Ethyl ether	88,941.20	J	103,976.50	J	ppbv
Formaldehyde	259.00	B	99.60	B	ug/m <sup>3</sup>
Heptanal	46.70		30.60		ug/m <sup>3</sup>
Hexanal	175.00		60.70		ug/m <sup>3</sup>
Methyl Chloride	906.00	B	598.00	B	ppbv
m-Tolualdehyde	24.90		13.40		ug/m <sup>3</sup>
Nitrous Oxide	465.00		202.00		ppmv
Nonanal	2.29	U	19.80		ug/m <sup>3</sup>
NOx	0.50		0.60		ppmv
Octanal	0.92	U	19.10		ug/m <sup>3</sup>
Oxygen	21.10		21.20		%
Pentanal	86.20		49.00		ug/m <sup>3</sup>
RDX	4.78	MAX			ug/m <sup>3</sup>
Toluene	22,400.00		18,100.00		ppbv
Total Hydrocarbons	400.00		1,248.00		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

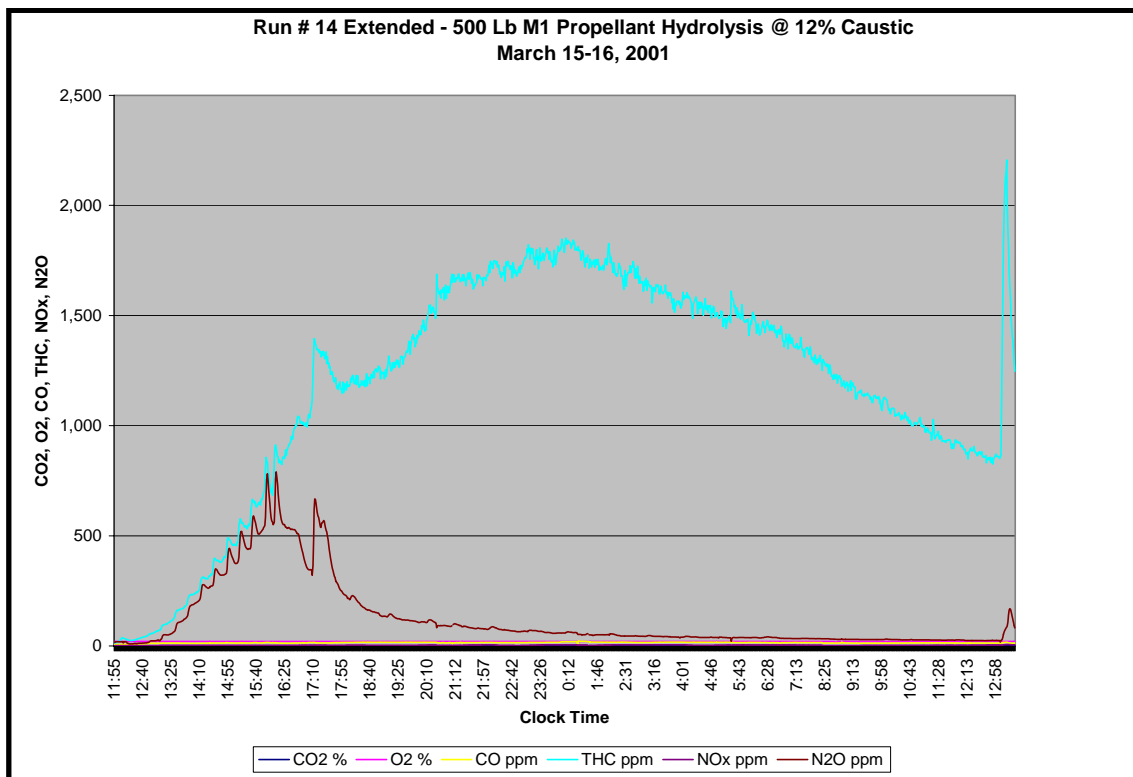


Figure 6-19. Run 14, Off-gas Production

The THC levels did not fall off until nearly 12 hours into the 24-hour run. The spike in the THC level at the ~1300 hour clock time was induced by increasing the agitation speed; thereby supporting the hypothesis that there is significant amounts of dissolved gas in the hydrolysate.

#### 6.2.2 Discussion & Analysis:

1. The end of run liquid analyses indicates that the destruction efficiency achieved approximately 6 hours after cessation of the feeding of M1 propellant to the reactor – 10 hours after the start of the run – ranged from 99.9988% to 100.00%. DNT was detected in the end of run analysis for Run 9.
2. The energetics loading for the four runs with M1 propellant is 6.8 - 8.2 weight-percent resulting in a total solids (dissolved and suspended) loading at the end of the run of between 12.7-to-29.6 weight-percent depending on the caustic strength.
3. The only "bad actor" detected in the hydrolysate is cyanide (possibly sodium cyanide) at a range of 29 to 95 ppm, increasing in concentration with increasing caustic strength. As stated in paragraph 6.1.2 above, the hydrolysis of energetics will produce cyanide and that the subsequent treatment of said hydrolysate using SCOW technology will adequately reduce the hazardous compound concentrations in the hydrolysate feeds well below levels of concern
4. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. The off gassing continued to increase after the addition of the propellant was completed (see Figures 6-14, 6-16, and 6-18), indicating that the reaction was progressing to completion in line with the liquid analysis data. However, the THCs showed no reduction and actually were increasing when the run point was terminated after approximately 10

hours. Run 14, the extended run was conducted to see if an endpoint could be reached regarding off gassing after 24-hours. At 23 hours into the 24-hour run, the agitator speed was increased to see if the off gassing would be effected, and immediately the THC's released increased dramatically (see Figure 6-19). It is conjectured that the off gassing is the results of dissolved gasses and the continued reaction of the caustic solution with the by-products of the destruction of the NC chain (M1 propellant contains 84% NC). Increasing the agitation simply allowed dissolved gasses to be released from the hydrolysate.

5. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
6. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. Foaming was not experienced with M1 propellant.
7. Examination of the off-gas characterization for the four runs indicates that trace amounts of TNT 1,3,5-trinitrobenzene, Dinitrotoluene (most likely from nitration of DNT used in the M1 propellant at a level of 9%) and HMX and RDX (most likely line residuals from the Composition B and B4 runs) were entrained in the gas stream during the addition phase of the process. All energetics disappeared once the M1 propellant addition was completed. Use of a condenser just above the reactor to drop any entrained materials back into the reactor should be effective.
8. The only significant "bad actors" identified in all four of the off-gas characterizations were toluene, xylene and benzene. These components and other in the off gas stream can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release.
9. The other major constituents of the off gassing were ammonia, acetone, acetaldehyde, and ethyl ether. These gasses can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release. The average range concentration of CO<sub>2</sub>, O<sub>2</sub>, CO, THC, NO<sub>x</sub> and N<sub>2</sub>O in the off gas stream during energetic addition for the three runs was: 0.03 - .04%, 21.2 – 21.3%, 0.0 – 2.0 ppmvd, 24.3 – 400.0 ppmvd, 0.5 – 0.7 ppmvd, 113 – 465 ppmvd, respectively and during digestion the concentration was: 0.03 - 0.04%, 21.2 – 21.3%, 1 - 5 ppmvd, 1,248 – 1,680 ppmvd, 0.0 – 1 ppmvd, 202 – 257 ppmvd, respectively.
10. The inorganic materials (metals) detected in the hydrolysate end of runs analysis are sourced from the sodium hydroxide stock feed that contains some of these components.

### 6.3. Unleaded M28 Propellant Hydrolysis Tests & Results (Runs 12 & 13).

The objective of these tests is to clearly determine and define the optimum operating parameters for the M28 propellant hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Pueblo Chemical Agent Disposal Facility for the destruction of propellants contained in the 115mm Rocket, Chemical Agent GB, M56; 115mm Rocket Warhead, Chemical Agent GB, M55; 115mm Rocket, Chemical Agent VX, M55; and 115mm Rocket Warhead, Chemical Agent GB, M55.

The inventory of unleaded M28 granular surrogate propellant (produced at Radford AAP to support the ACWA program) was only sufficient to support two test runs. The M28 surrogate propellant was produced in granulated form as opposed to the cast rocket grain form used in the end item because of cost. Both a leaded version (to the military specification) and an unleaded version (to avoid producing a lead containing waste) of the M28 surrogate propellant were produced at Radford AAP. Figure 6-20 below illustrates the difference between the granulated surrogate propellant used for test purposes and the actual configuration of the cast M28 propellant grains found in the end items. The grains segments pictured were sourced from the propellant surveillance program at Picatinny Arsenal and used to support the grinding study. Consequently, the grains do not have the fluted perforation as the actual propellant grain configuration produced for the end item is shown in Figure 6-21.

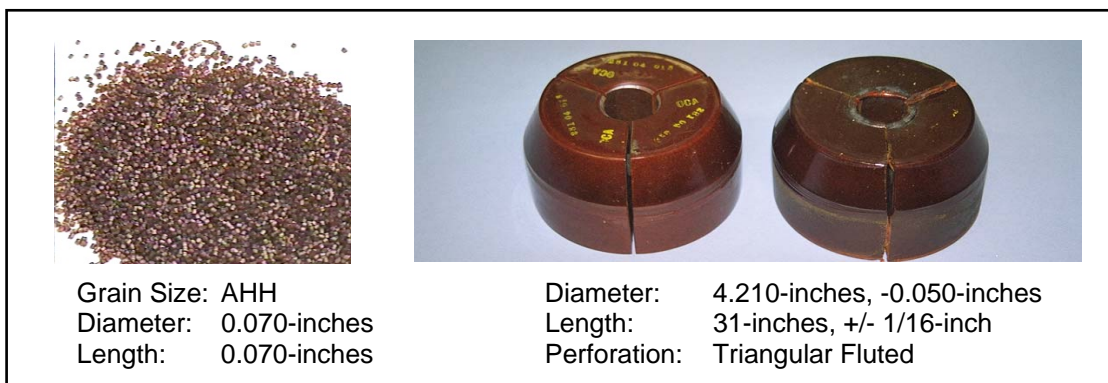


Figure 6-20. M28 Surrogate propellant and Surveillance Propellant Grain Segments

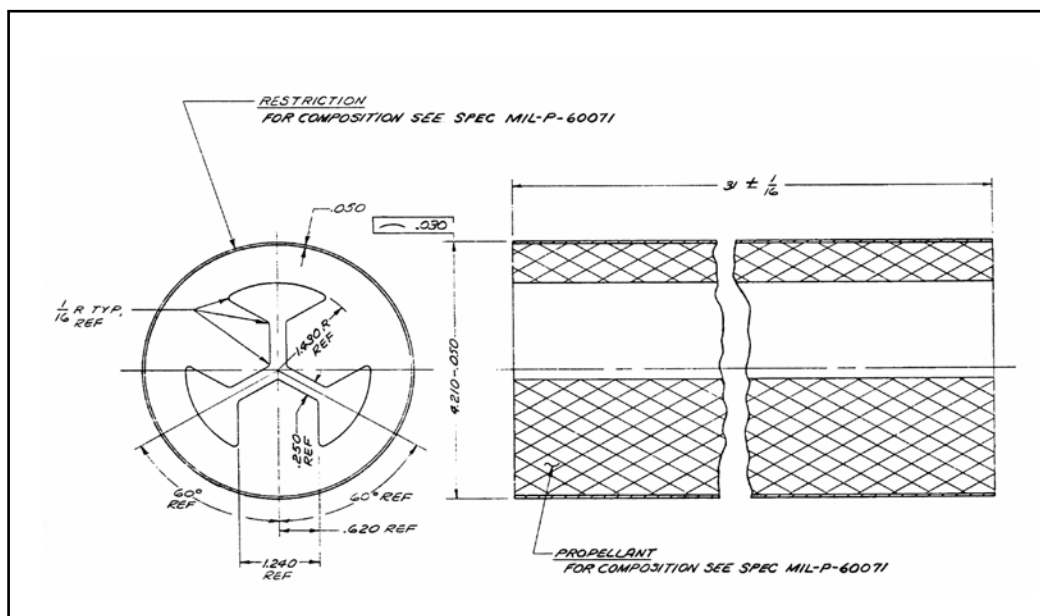


Figure 6-21. M28 Propellant Grain for 115mm Rocket Motor

The table below identifies the process operating and control parameters for Runs 12 and 13.

Table 6-15. M28 Propellant (Unleaded) Test Parameters

Operating Condition	Run 12	Run 13
M28 Feed Rate, lbs/hr		
1 <sup>st</sup> hour	50	50
2 <sup>nd</sup> hour	100	100
3 <sup>rd</sup> hour	150	150
4th hour	200	200
Caustic Soda Concentration, wt%	11.3	20
Caustic Soda Feed, gal	700	700
Reactor Operating Temperature, °C	87	87
Agitation Speed, RPM	70	70
Date Conducted	3/9/2001	3/13/2001

The following charts present the process operating and control parameters for hydrolysis of M28 propellant:

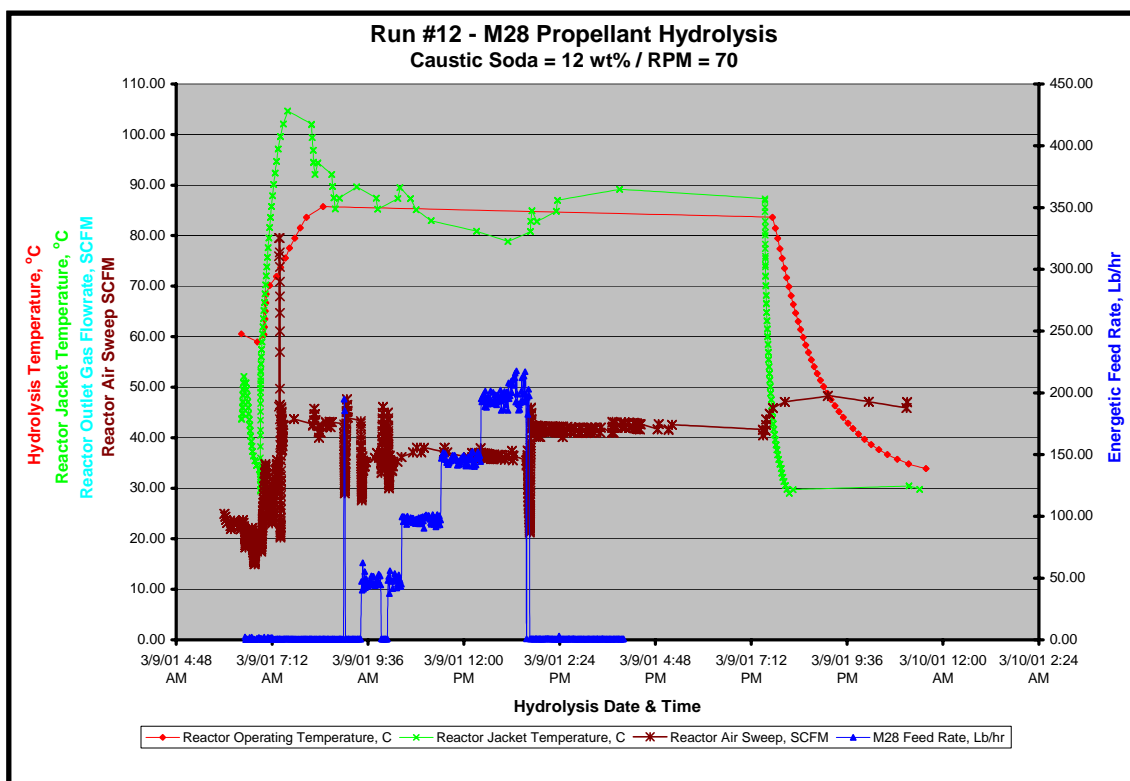


Figure 6-22. Run 12, Process Operating and Control Parameters

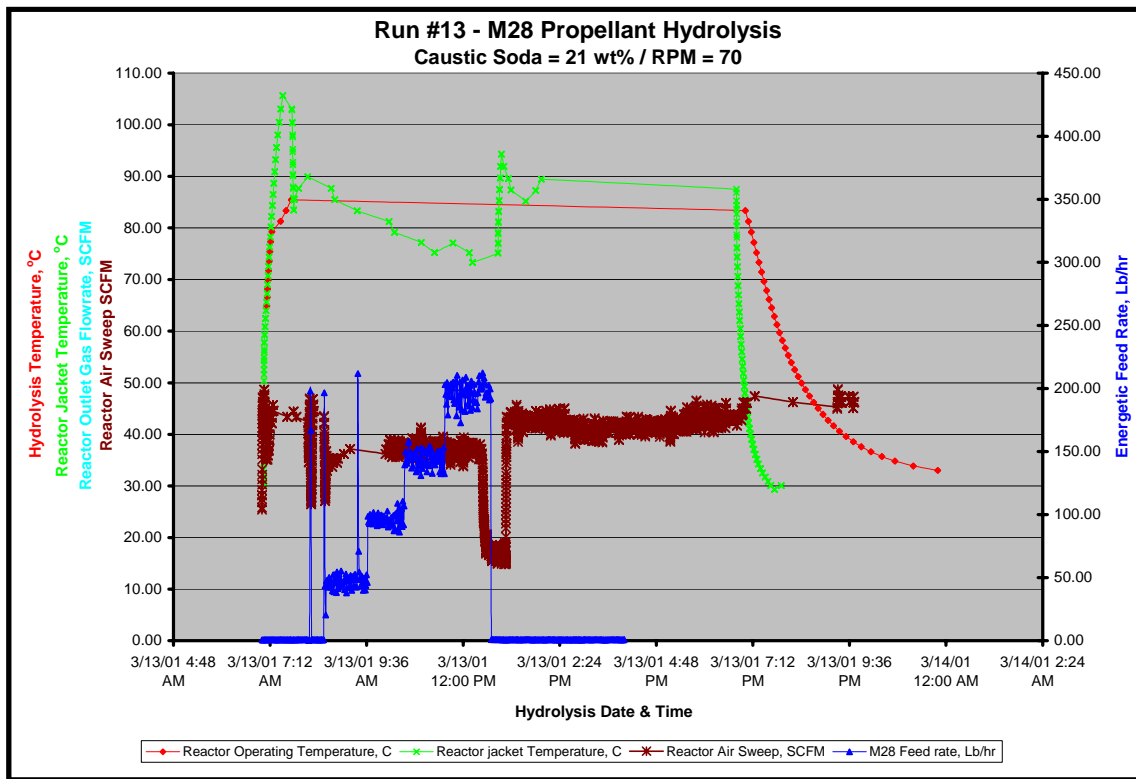


Figure 6-23. Run 13, Process Operating and Control Parameters

### 6.3.1 Tests Results:

The following plots represent the destruction of M28 propellant as a function of reactor residence time.

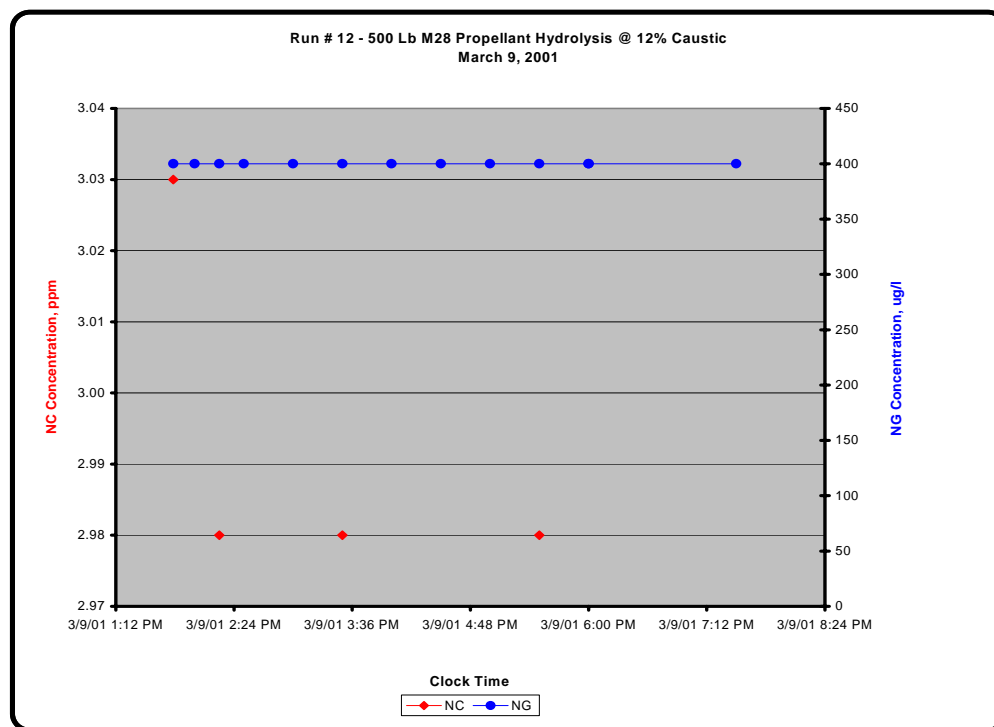


Figure 6-24. Run 12, Mid-Run Destruction Efficiency

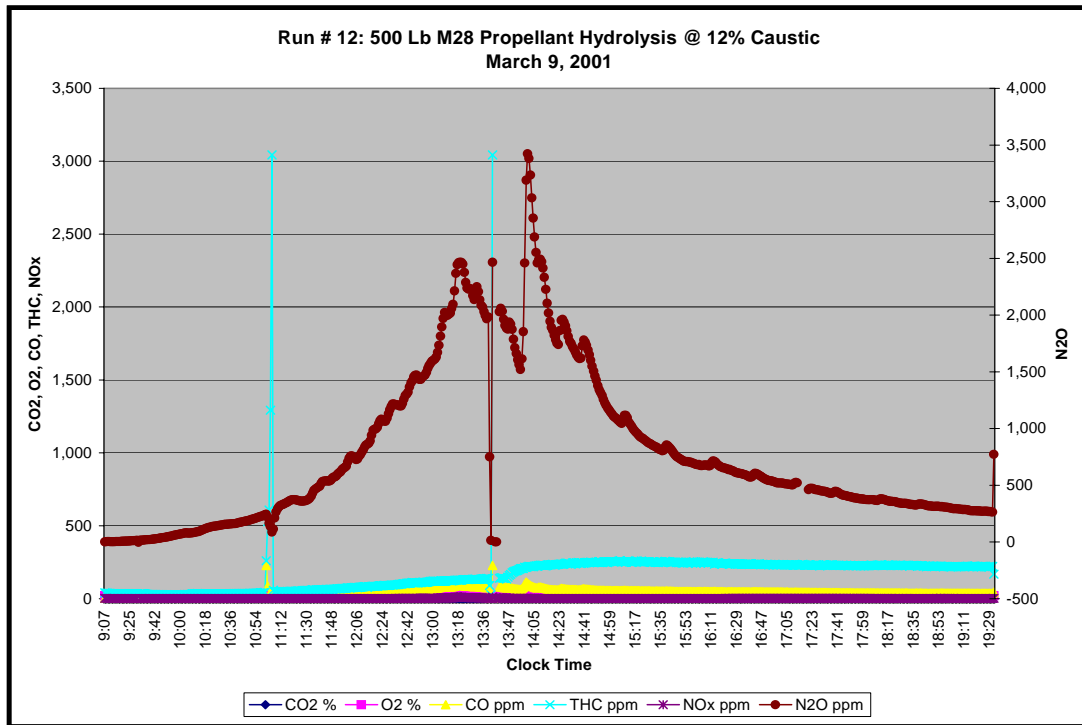


Figure 6-25. Run 12, Off-gas Production



Table 6-16. Run 12, M28 Propellant (Unleaded) End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	14,600.00	mg/l	14,600.00	
Aluminum	487.00	ug/l	0.487	
Ammonia	105.00	mg/l	105.00	
Barium	99.30	ug/l	0.0993	
Calcium	38,200.00	ug/l	38.2	
Chloride	32.30	mg/l	32.30	
Chromium	126.00	ug/l	0.126	
Copper	1,600.00	ug/l	1.6	
Cyanide (Sodium Cyanide)	208,000.00	ug/l	208	
Fluoride	949.00	mg/l	949.00	
Formate	2,360.00	mg/l	2,360.00	
Magnesium	8,000.00	ug/l	8	
Molybdenum	27.80	ug/l	0.0278	J
Nickel	176.00	ug/l	0.176	
Nitrate-N	2,090.00	mg/l	2,090.00	
Nitrite-N	4,760.00	mg/l	4,760.00	
N-Nitrosodiphenylamine	2,700.00	ug/l	2.7	J
Phenol	920.00	ug/l	0.92	J
Phosphorus	490.00	ug/l	0.49	J
Potassium	8,890.00	ug/l	8.89	J
Sodium	50,890,000.00	ug/l	50890	
Sulfate	135.00	mg/l	135.00	
Zinc	268.00	ug/l	0.268	
TIC	1,127.50	mg/l	1,127.50	
TOC	16,375.00	mg/l	16,375.00	
COD	46,300.00	mg/l	46,300.00	
Total Suspended Solids	740.00	mg/l	740.00	
Total Dissolved Solids	153,000.00	mg/l	153,000.00	
Normality as NaOH	1.35	n		
Density	1.10	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-17. Run 12, M28 Propellant (Unleaded) Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1-Butanol	3,456.50	J	725.00	J	ppbv
2-Butanone	722.00	U	4,030.00		ppbv
Acetaldehyde	16,600.00	D	18,400.00	D	ug/m <sup>3</sup>
Acetone	29,100.00		34,000.00		ppbv
Acetonitrile	1,702.30	J			ppbv
Ammonia	159,000.00		1,070,000.00		ug/m <sup>3</sup>
Benzene	184.00		390.00		ppbv
Butanal	325.00		1,160.00		ug/m <sup>3</sup>
Carbon Dioxide	0.04		0.05		%
Carbon Monoxide	34.00		45.00		ppmv
Chloroform	21.60		60.00	U	ppbv
Crotonaldehyde	435.00		8.22		ug/m <sup>3</sup>
Cyanide	0.01		0.08		mg/m <sup>3</sup>
Cyclohexanone	64.70		103.00		ug/m <sup>3</sup>
Ethanol	87.80	J			ppbv
Formaldehyde	182.00	B	63.60	B	ug/m <sup>3</sup>
Heptanal	78.80		50.70		ug/m <sup>3</sup>
Hexanal	134.00		57.30		ug/m <sup>3</sup>
Methylene Chloride	37.60		435.00		ppbv
m-Tolualdehyde	12.70		33.40		ug/m <sup>3</sup>
NG	1,490.00				ug/m <sup>3</sup>
Nitrous Oxide	766.00		857.00		ppmv
Nonanal	40.70		1.90	U	ug/m <sup>3</sup>
NOx	1.40		1.00		ppmv
Octanal	35.40		0.77	U	ug/m <sup>3</sup>
Octane	80.47			J	ppbv
Oxygen	21.20		21.10		%
Pentanal	0.54	U	32.10		ug/m <sup>3</sup>
Toluene	37.50		60.00	u	ppbv
Total Hydrocarbons	103.00		321.00		ppmv

J = Estimated Value; concentration is below limit of quantification

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

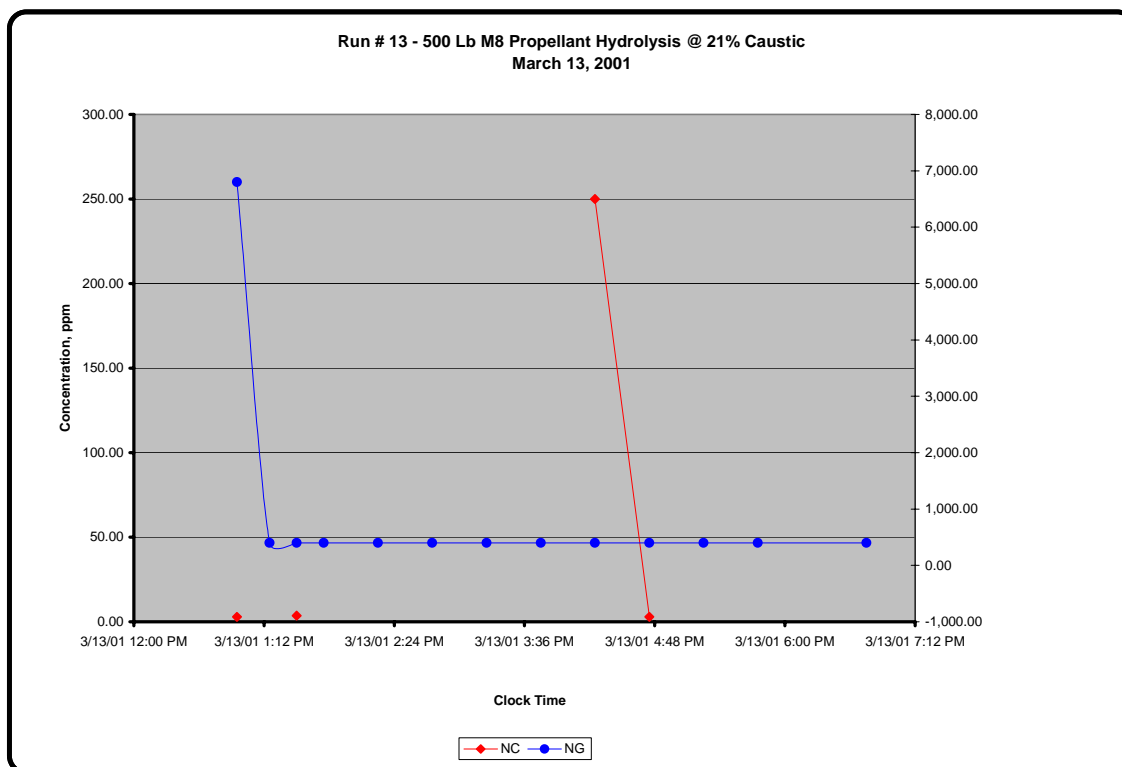


Figure 6-26. Run 13, Mid-Run Destruction Efficiency

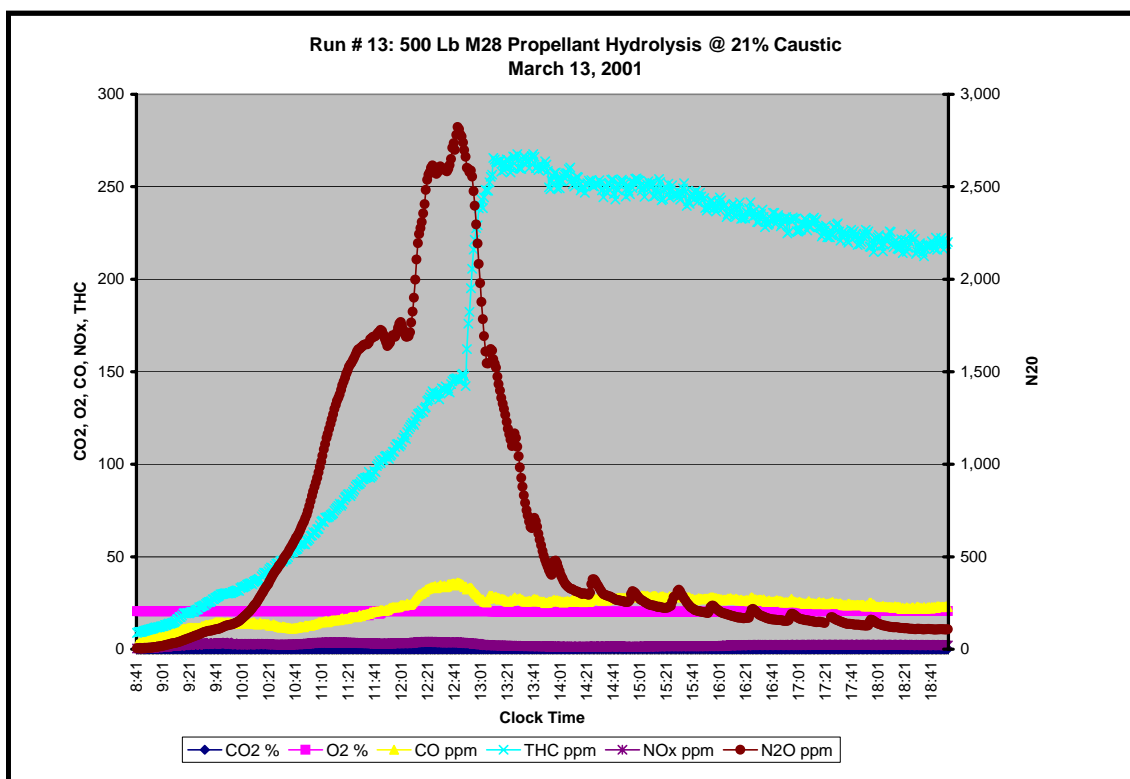


Figure 6-27. Run 13, Off-gas Production

Table 6-18. Run 13, M28 Propellant (Unleaded) End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	10,100.00	mg/l	10,100.00	
Aluminum	236.00	ug/l	0.24	J
Ammonia	95.50	mg/l	95.50	
Barium	124.00	ug/l	0.12	
bis(2-Ethylhexyl)phthalate	330.00	ug/l	0.33	J
Calcium	34,800.00	ug/l	34.80	
Carbazole	610.00	ug/l	0.61	J
Chloride	304.00	mg/l	304.00	
Chromium	195.00	ug/l	0.20	
Cobalt	78.40	ug/l	0.08	
Copper	1,310.00	ug/l	1.31	
Cyanide (Sodium Cyanide)	324,000.00	ug/l	324.00	
Fluoride	1,060.00	mg/l	1,060.00	
Formate	2,440.00	mg/l	2,440.00	
Iron	4,970.00	ug/l	4.97	
Magnesium	7,160.00	ug/l	7.16	
Manganese	54.70	ug/l	0.05	
Molybdenum	72.90	ug/l	0.07	
Nickel	380.00	ug/l	0.38	
Nitrate-N	2,070.00	mg/l	2,070.00	
Nitrite-N	4,930.00	mg/l	4,930.00	
N-Nitrosodiphenylamine	1,900.00	ug/l	1.90	J
o-Phosphate-P	488.00	mg/l	488.00	
Phosphorus	92.30	ug/l	0.09	J
Potassium	18,700.00	ug/l	18.70	
Sodium	106,000,000.00	ug/l	106,000.00	
Sulfate	162.00	mg/l	162.00	
Zinc	348.00	ug/l	0.35	
TIC	1,325.00	mg/l	1,325.00	
TOC	17,200.00	mg/l	17,200.00	
COD	36,300.00	mg/l	36,300.00	
Total Suspended Solids	470.00	mg/l	470.00	
Total Dissolved Solids	262,000.00	mg/l	262,000.00	
Normality as NaOH	3.80	n		
Density	1.19	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-19. Run 13, M28 Propellant (Unleaded) Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1-Butanol	77.73	J			ppbv
2-Butanone	850.00		1,140.00	U	ppbv
Acetaldehyde	10,300.00	D	6,090.00	D	ug/m <sup>3</sup>
Acetone	22,000.00		10,600.00		ppbv
Ammonia	198,000.00		1,120,000.00		ug/m <sup>3</sup>
Benzene	602.00		174.00		ppbv
Bromodichloromethane	22.20		30.00	U	ppbv
Butanal	214.00		407.00		ug/m <sup>3</sup>
Carbon Dioxide	0.02		0.06		%
Carbon Monoxide	10.00		19.00		ppmv
Chloroform	33.00		30.00	U	ppbv
Cyanide	0.00	U	0.04		mg/m <sup>3</sup>
Cyclohexanone	63.50		47.10		ug/m <sup>3</sup>
Dibromochloromethane	13.10		30.00	U	ppbv
Formaldehyde	66.50	B	20.20	B	ug/m <sup>3</sup>
Heptanal	46.90		21.60		ug/m <sup>3</sup>
Hexanal	136.00		25.60		ug/m <sup>3</sup>
Methylene Chloride	214.00	B	266.00	B	ppbv
m-Tolualdehyde	3.15	J	10.90		ug/m <sup>3</sup>
NG	4,030.00				ug/m <sup>3</sup>
Nitrous Oxide	978.00		401.00		ppmv
Nonanal	42.70		1.31	U	ug/m <sup>3</sup>
NOx	2.10		1.20		ppmv
Octanal	35.40		0.53	U	ug/m <sup>3</sup>
Oxygen	21.20		21.10		%
Phenol			18.90	J	ppbv
Toluene	11.50	U	85.50		ppbv
Total Hydrocarbons	95.70		334.70		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank.

### 6.3.2 Discussion & Analysis:

1. The end of run liquid analyses indicates that the desired 100.00% destruction efficiency was achieved approximately 3 hours after cessation of the feeding of M28 propellant to the reactor – 7 hours after the start of the run.
2. The energetics loading for the four runs with M28 unleaded propellant is 7.1 – 7.9 weight-percent resulting in a total solids (dissolved and suspended) loading at the end of the run of between 15.4-to-26.3 weight-percent depending on the caustic strength.
3. The only “bad actor” detected in the hydrolysate is cyanide (possibly sodium cyanide) at a range of 208 to 324 ppm, increasing in concentration with increasing caustic strength. As stated in paragraph 6.1.2 above, the hydrolysis of energetics will produce cyanide and that the subsequent treatment of said hydrolysate using SCOW technology will adequately reduce the hazardous compound concentrations in the hydrolysate feeds well below levels of concern.
4. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. With the exception of THC<sub>s</sub>, the off gassing quickly fell-off after the addition of the propellant was completed (see Figures 6-25 and 6-27), indicating that the reaction was progressing to conclusion in line with the liquid analysis data. It was conjectured that the THC off gassing was the results of dissolved gasses being liberated and the continued reaction of the caustic solution with the by-products of the destruction of the NC chain.
5. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
6. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. Foaming was not experienced with M28 propellant.
7. Examination of the off-gas characterization for the two runs indicates that NG vapor was detected in the gas stream only during the addition phase of the process. NG has a measurable vapor pressure at ambient, therefore one would expect NG to come-off as part of the off-gassing stream. Use of a condenser to drop any entrained materials back into the reactor should be effective; however, the condenser should be designed for potential service with NG vapors and cleaned accordingly when the system is decommissioned from service.
8. The major constituents of the off gassing were acetaldehyde, acetone, and ammonia. These gasses can be effectively treated with a scrubber system, with the effluent water from the scrubber then processed through the SCWO system as the final treatment step before release. The average concentration of CO<sub>2</sub>, O<sub>2</sub>, CO, THC, NO<sub>x</sub> and N<sub>2</sub>O in the off gas stream during energetic addition for the two runs was: 0.04%, 21.2%, 34 ppmvd, 103 ppmvd, 1.4 ppmvd, 766 ppmvd, respectively and during digestion the concentration was: 0.05%, 21.1%, 45 ppmvd, 321 ppmvd, 1.0 ppmvd, 857 ppmvd, respectively.
9. The inorganic materials (metals) detected in the hydrolysate end of runs analysis are sourced from the sodium hydroxide stock feed that contains some of these components.

## 6.4 Tetrytol Explosive Hydrolysis Tests & Results (Runs 15, 16, and 17).

The objective of these tests is to clearly determine and define the optimum operating parameters for the Tetrytol and Tetrytol explosive hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Pueblo and the Blue Grass Chemical Agent Disposal Facility for the destruction of explosives contained in the 4.2-inch Cartridge, Chemical Agent HT and HD, M2 and M2A1; 105mm Projectile, Chemical Agent HD, M60; and 155mm Projectile, Chemical Agent HD, M104 and M110.

The table below identifies the process operating parameters for Runs 15, 16 and 17. Each test was conducted with 350-pounds of Tetrytol as opposed to 500-pounds due to limited supplies over a three hour addition period.

Table 6-20. Tetrytol Explosive Test Parameters

Operating Condition	Run 15	Run 16	Run 17
Tetrytol Feed Rate, lbs/hr			
1 <sup>st</sup> hour	50	50	50
2 <sup>nd</sup> hour	100	100	100
3 <sup>rd</sup> hour	200	200	200
Caustic Soda Concentration, wt%	12	21	26
Caustic Soda Feed, gal	700	700	700
Reactor Operating Temperature, °C	87	87	87
Agitation Speed, RPM	80	80	80
Date Conducted	3/26/2001	3/28/2001	3/30/2001

The following charts represent the process operating and control parameters for the hydrolysis for Tetrytol explosives:

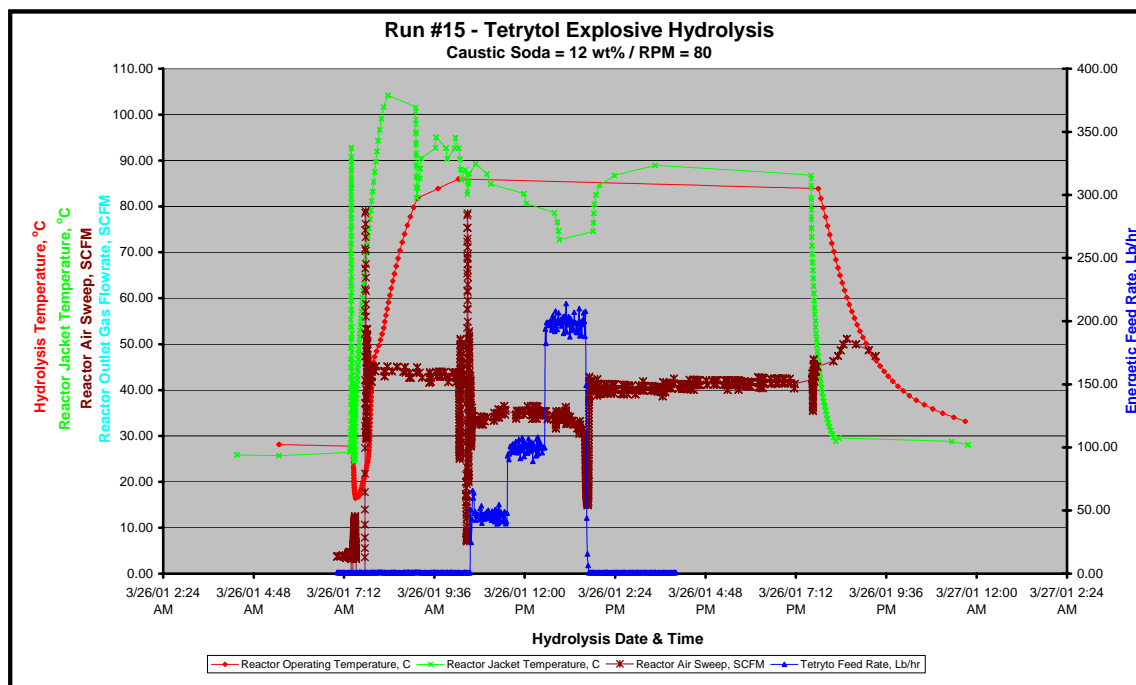


Figure 6-28. Run 15, Process Operating and Control Parameters

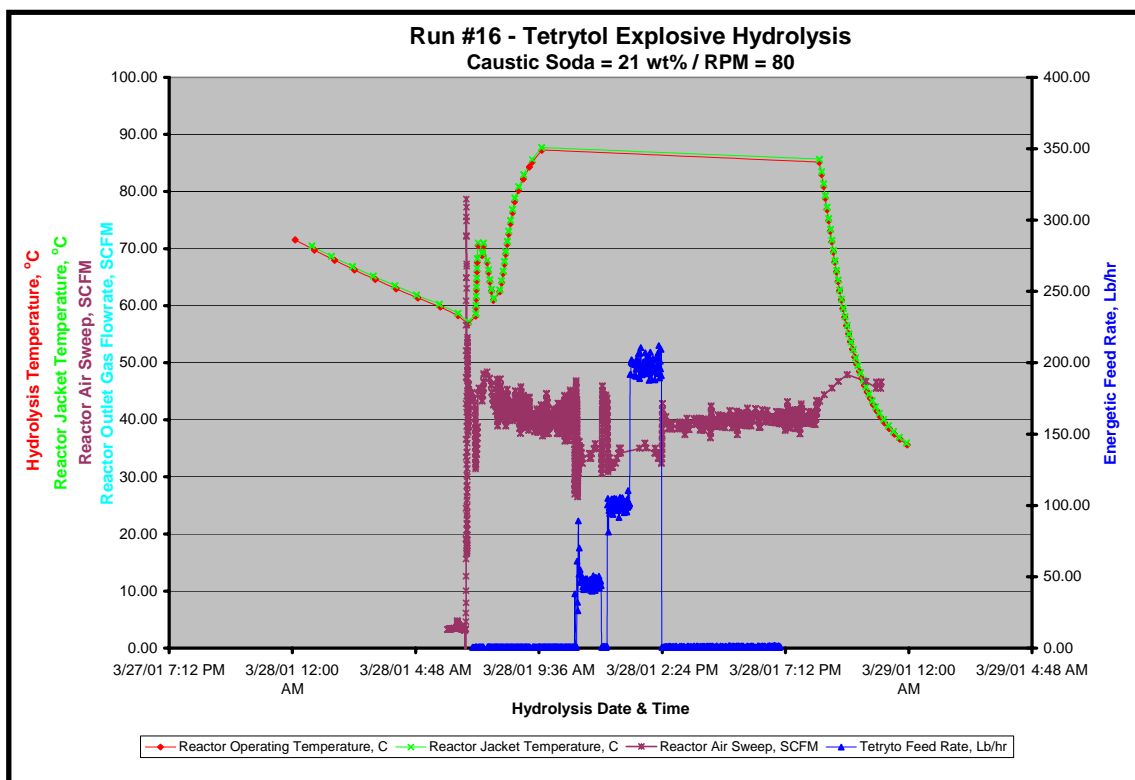


Figure 6-29. Run 16, Process Operating and Control Parameters

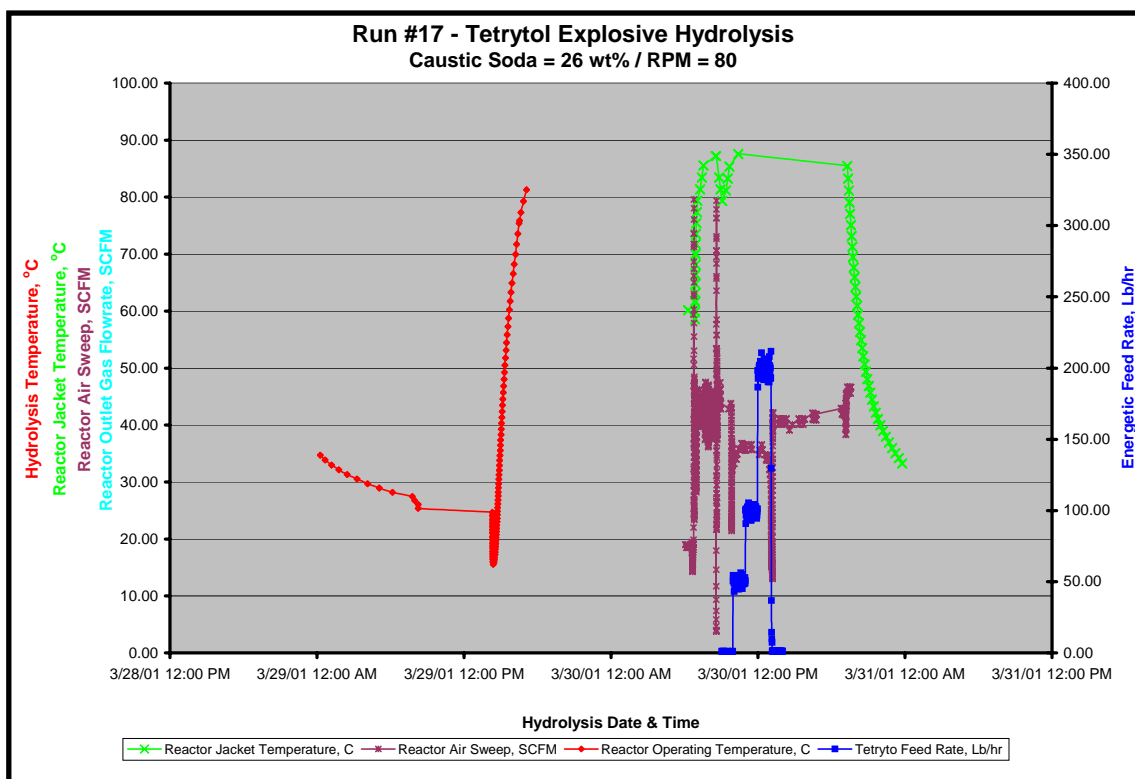


Figure 6-30. Run 17, Process Operating and Control Parameters



#### 6.4.1 Tests Results:

The following plots represent the destruction of Tetrytol explosive as a function of reactor residence time.

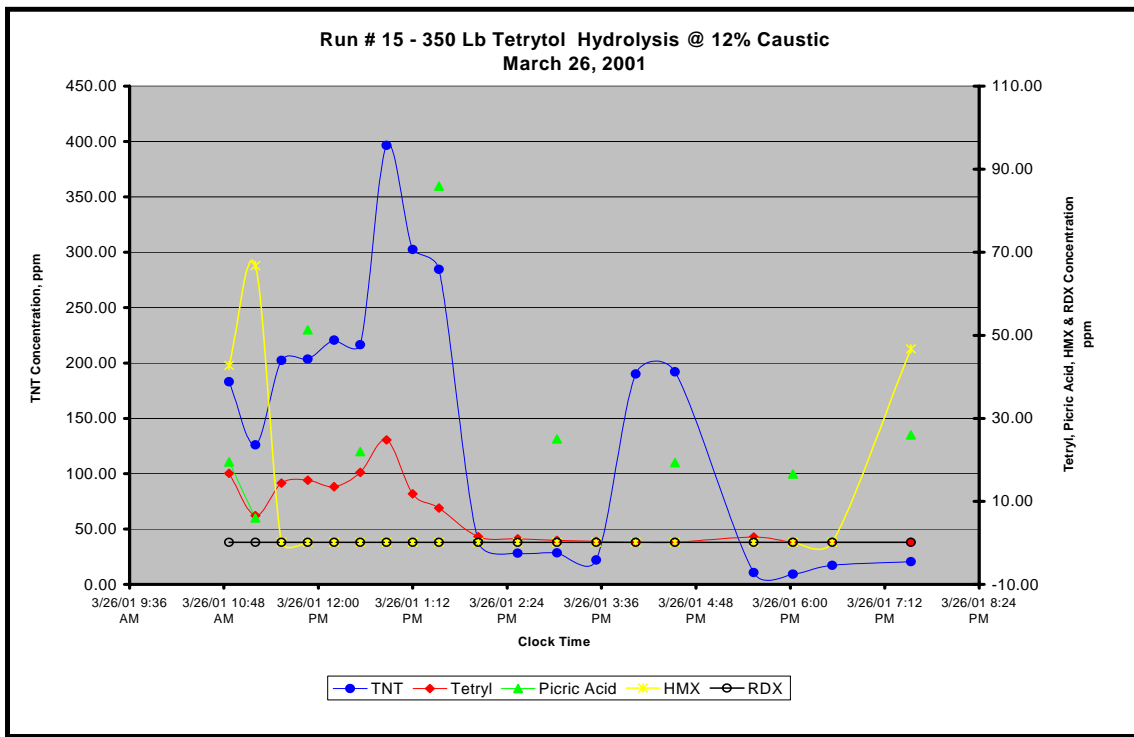


Figure 6-31. Run 15, Mid-Run Destruction Efficiency

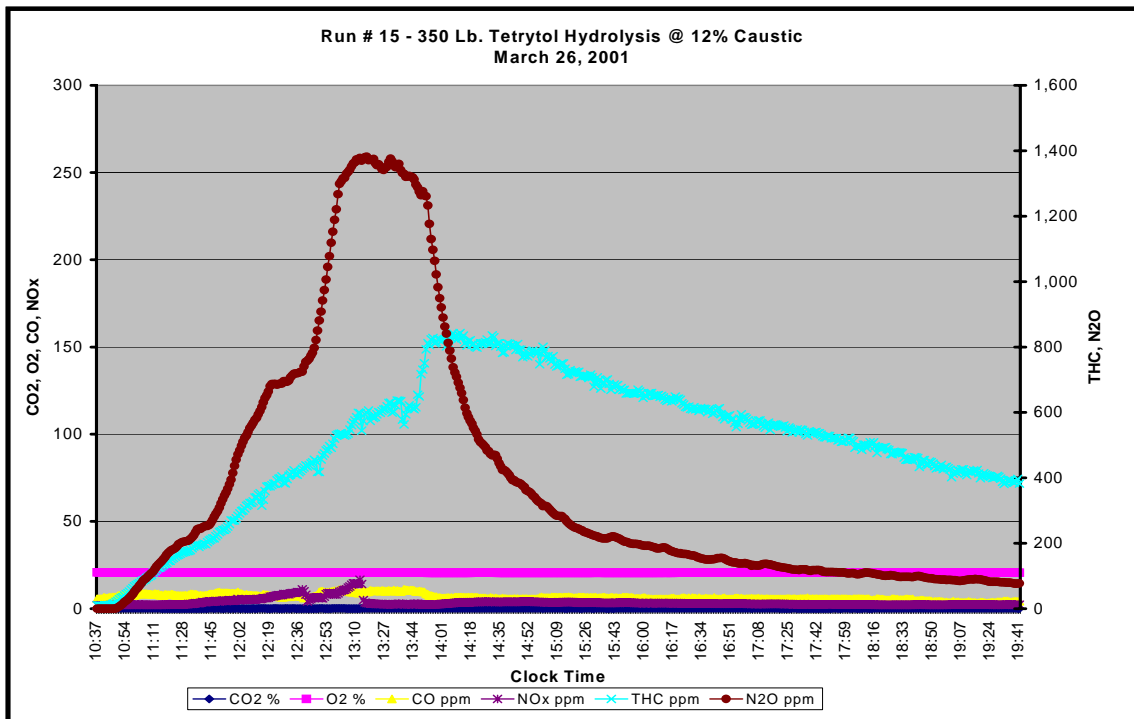


Figure 6-32. Run 15, Off-gas Production

Table 6-21. Run 15, Tetrytol Explosive End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
2-Fluoro-4-nitrophenol	1,100.00	ug/l	1.10	J
Acetate	438.00	mg/l	438.00	
Ammonia	1,260.00	mg/l	1,260.00	
Calcium	28,300.00	ug/l	28.30	
Cyanide (Sodium Cyanide)	259,000.00	ug/l	259.00	
Diethylphthalate	310.00	ug/l	0.31	J
Formate	2,250.00	mg/l	2,250.00	
Magnesium	7,310.00	ug/l	7.31	
Nitrate-N	29.60	mg/l	29.60	
Nitrite-N	3,460.00	mg/l	3,460.00	
o-Phosphate-P	16.10	mg/l	16.10	
Phosphorus	770.00	ug/l	0.77	J
Sodium	51,300,000.00	ug/l	51,300.00	
Sulfate	400.00	mg/l	400.00	
Zinc	279.00	ug/l	0.28	
TIC	2,235.00	mg/l	2,235.00	
TOC	11,342.50	mg/l	11,342.50	
COD	30,800.00	mg/l	30,800.00	
Total Suspended Solids	200.00	mg/l	200.00	
Total Dissolved Solids	213,000.00	mg/l	213,000.00	
Normality as NaOH	1.60	n		
Density	1.10	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-22. Run 15, Tetrytol Explosive Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	52.2000	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	0.3880	MAX			ug/m <sup>3</sup>
1-Butanol	1,198.5000	J	228.1000	J	ppbv
2,4,6-Trinitrotoluene	80.7000	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	15.2000	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	0.1240	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	0.4350	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	0.6810	MAX			ug/m <sup>3</sup>
Acetaldehyde	10.6000	B	8.0200	B	ug/m <sup>3</sup>
Acetone	1,980.0000	B	2,580.0000	B	ppbv
Ammonia	46,000.0000		178,000.0000		ug/m <sup>3</sup>
Bromomethane	164.0000		112.0000		ppbv
Butanal	0.0971	J	0.1970		ug/m <sup>3</sup>
Carbon Dioxide	0.0000		0.0000		%
Carbon Monoxide	3.0000		0.0000		ppmv
Chloroform	37.3000		15.5000	U	ppbv
Chloromethane	27.5000		25.2000		ppbv
Crotonaldehyde	0.3250	J	0.0534	J	ug/m <sup>3</sup>
Cyanide	0.0015		0.0005		ug/m <sup>3</sup>
Cyclohexanone	0.2050	J	0.0021	U	ug/m <sup>3</sup>
Ethylenimine			677.9000	J	ppbv
Formaldehyde	49.1000	J	63.6000	J	ug/m <sup>3</sup>
Heptanal	0.0883	J	0.0049	U	ug/m <sup>3</sup>
Hexanal	0.1730	J	0.0063	U	ug/m <sup>3</sup>
Methyl Chloride	116.0000	B	23.3000	B	ppbv
m-Tolualdehyde	4.2200		0.1490	J	ug/m <sup>3</sup>
Nitrous Oxide	634.0000		248.0000		ppmv
Nonanal	0.1400	J	0.0329	J	ug/m <sup>3</sup>
NOx	2.8000		0.7000		ppmv
Octanal	0.0852	J	0.0161	J	ug/m <sup>3</sup>
Oxygen	21.4000		21.2000		%
Pentanal	1.0100		0.0035	U	ug/m <sup>3</sup>
Tetryl	14.0000	MAX			ug/m <sup>3</sup>
Toluene	49.8000		39.1000		ppbv
Total Hydrocarbons	492.0000		915.0000		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank.

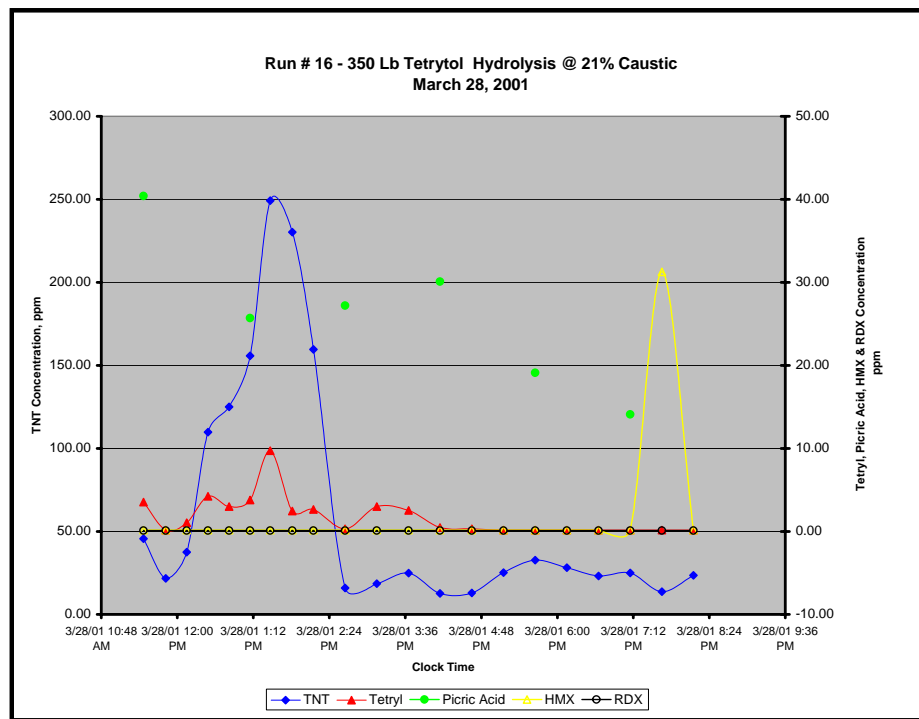


Figure 6-33. Run 16, Mid-Run Composition B4 Destruction Efficiency

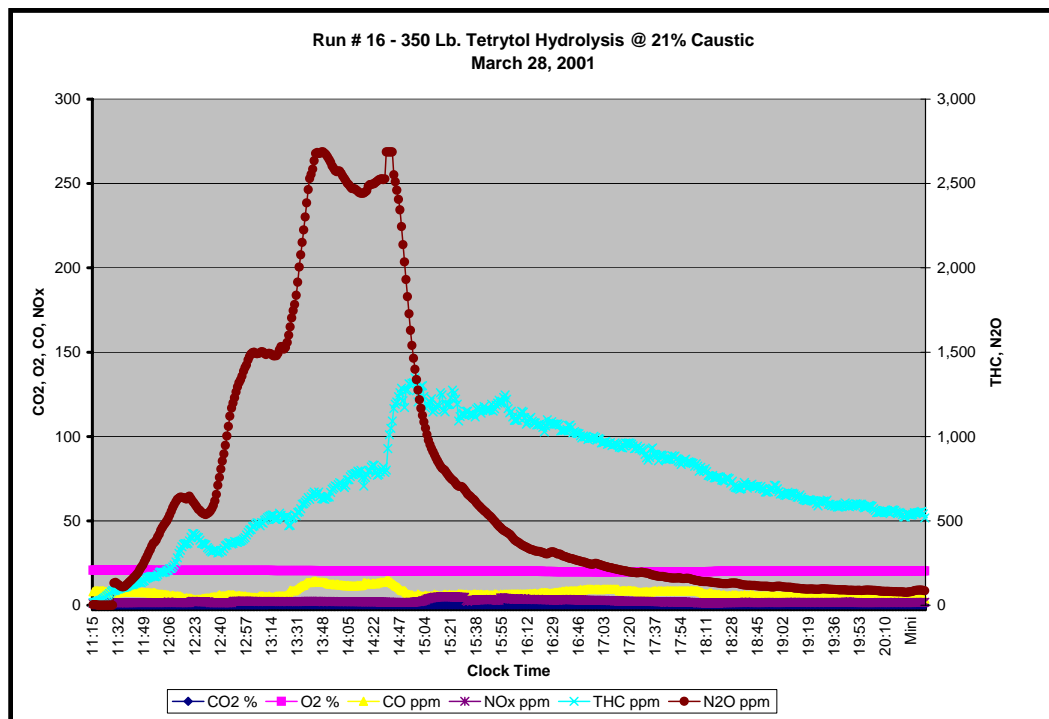


Figure 6-34. Run 16, Off-gas Production

Table 6-23. Run 16, Tetrytol Explosive End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
2-Fluoro-4-nitrophenol	1,400.00	ug/l	1.40	J
Acetate	566.00	mg/l	566.00	
Ammonia	1,270.00	mg/l	1,270.00	
bis(2-Ethylhexyl)phthalate	280.00	ug/l	0.28	J
Calcium	21,600.00	ug/l	21.60	
Cyanide (Sodium Cycnide)	315,000.00	ug/l	315.00	
Diethylphthalate	300.00	ug/l	0.30	J
Formate	2,930.00	mg/l	2,930.00	
HMX	28,495.00	ug/l	28.50	
Magnesium	6,830.00	ug/l	6.83	
Nitrate-N	44.60	mg/l	44.60	
Nitrite-N	3,210.00	mg/l	3,210.00	
o-Phosphate-P	29.00	mg/l	29.00	
Phosphorus	815.00	ug/l	0.82	J
Picric Acid	73.10	mg/l	73.10	
Potassium	180,000.00	ug/l	180.00	
Sodium	102,000,000.00	ug/l	102,000.00	
Sulfate	476.00	mg/l	476.00	
TNT	14,397.00	ug/l	14.40	
Zinc	315.00	ug/l	0.32	
TIC	2,135.00	mg/l	2,135.00	
TOC	12,475.00	mg/l	12,475.00	
COD	30,200.00	mg/l	30,200.00	
Total Suspended Solids	200.00	mg/l	200.00	
Total Dissolved Solids	251,000.00	mg/l	251,000.00	
Normality as NaOH	3.20	n		
Density	1.21	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-24. Run 16, Tetrytol Explosive Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	0.5540	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	0.5430	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	80.0000	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	12.4000	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	0.1260	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	0.3630	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	0.5090	MAX			ug/m <sup>3</sup>
Acetaldehyde	12.2000	B	1.7800	B	ug/m <sup>3</sup>
Acetone	1,690.0000	B	1,030.0000		ppbv
Ammonia	59,100.0000		221,000.0000		ug/m <sup>3</sup>
Bromomethane	52.8000		22.5000	U	ppbv
Butanal	0.3950		0.0394	J	ug/m <sup>3</sup>
Carbon Dioxide	0.0000		0.0000		%
Carbon Monoxide	0.0000		0.0000		ppmv
Chloroform	40.4000		15.0000	U	ppbv
Crotonaldehyde	0.4100		0.1560		ug/m <sup>3</sup>
Cyanide	0.0010		0.0004		ug/m <sup>3</sup>
Cyclohexanone	0.0292	J	0.0015	U	ug/m <sup>3</sup>
Ethylenimine			4,020.0000	J	ppbv
Formaldehyde	21.8000	B	18.4000	B	ug/m <sup>3</sup>
Heptanal	0.2670	J	0.0033	U	ug/m <sup>3</sup>
Hexanal	1.9900		0.0662	J	ug/m <sup>3</sup>
Methyl Chloride	30.0000	U	32.6000	B	ppbv
m-Tolualdehyde	0.3320		0.0042		ug/m <sup>3</sup>
Nitrous Oxide	1,279.0000		86.0000		ppmv
Nonanal	0.1630	J	0.0383	J	ug/m <sup>3</sup>
NOx	1.0000		0.9000		ppmv
Octanal	0.1230	J	0.0196	J	ug/m <sup>3</sup>
Oxygen	21.1000		20.8000		%
Pentanal	1.2200		0.0279	J	ug/m <sup>3</sup>
Tetryl	11.3000	MAX			ug/m <sup>3</sup>
Toluene	14.7000		15.0000	U	ppbv
Total Hydrocarbons	601.0000		755.0000		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

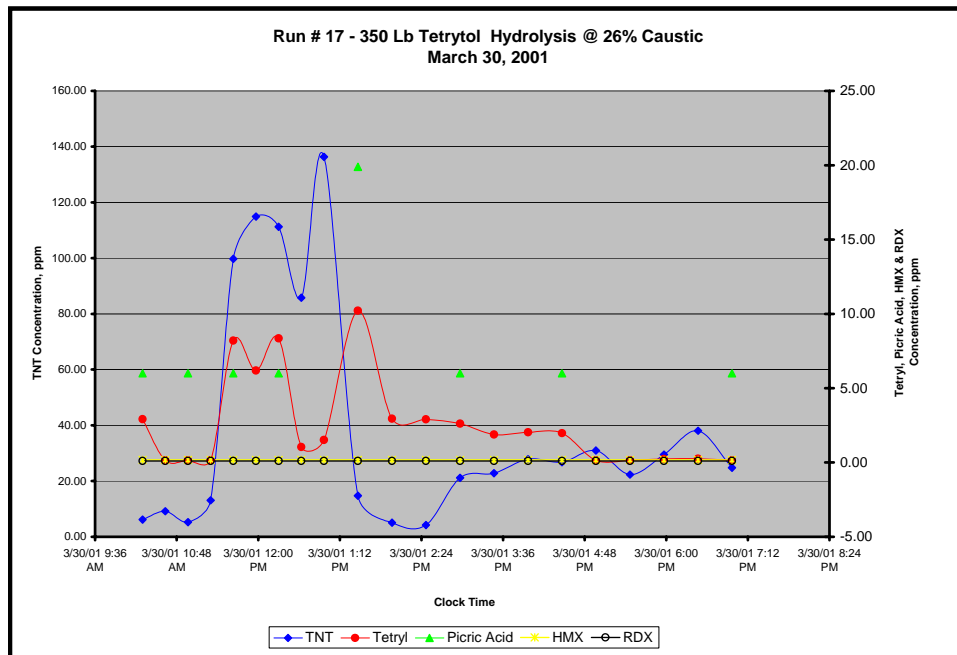


Figure 6-35. Run 17, Mid-Run Tetrytol Explosive Destruction Efficiency

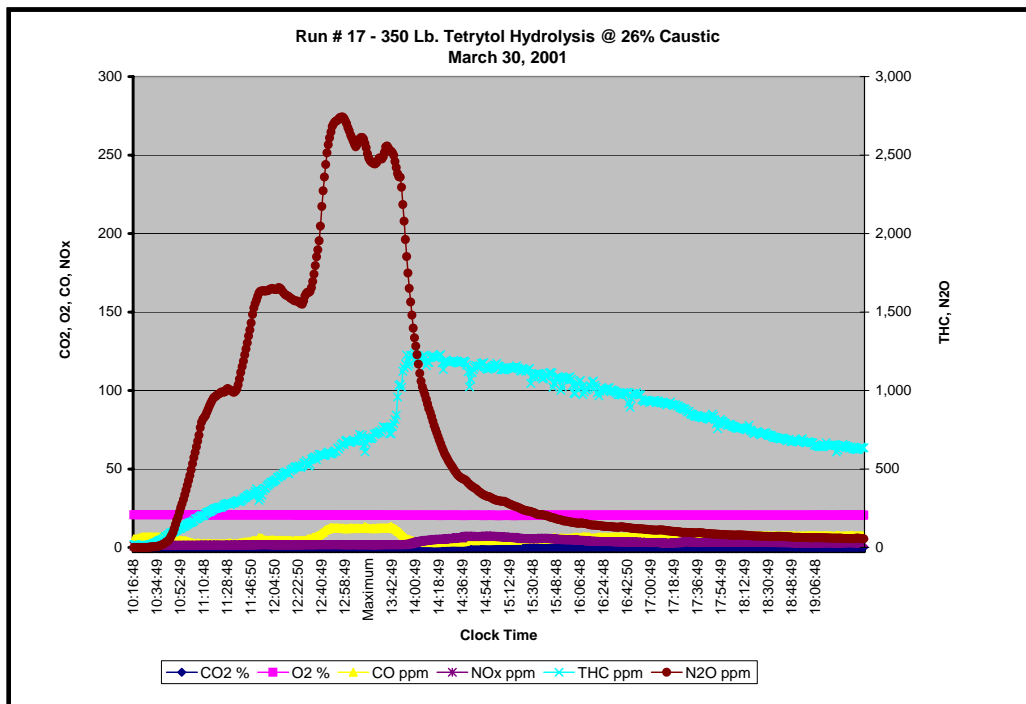


Figure 6-36. Run 17, Off-gas Production

Table 6-25. Run 17, Tetrytol Explosive End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	719.00	mg/l	719.00	
Ammonia	955.00	mg/l	955.00	
Barium	256.00	ug/l	0.26	
Calcium	17,900.00	ug/l	17.90	
Copper	521.00	ug/l	0.52	
Cyanide (Sodium Cyanide)	705,000.00	ug/l	705.00	
Fluoride	1,060.00	mg/l	1,060.00	
Formate	3,660.00	mg/l	3,660.00	
HMX	37,577.00	ug/l	37.58	
Magnesium	6,540.00	ug/l	6.54	
Molybdenum	59.90	ug/l	0.06	
Nitrate-N	30.10	mg/l	30.10	
Nitrite-N	2,740.00	mg/l	2,740.00	
o-Phosphate-P	30.20	mg/l	30.20	
Picric Acid	39.10	mg/l	39.10	
Potassium	122,000.00	ug/l	122.00	
Sodium	116,000,000.00	ug/l	116,000.00	
Sulfate	273.00	mg/l	273.00	
TNT	28,338.00	ug/l	28.34	
Zinc	333.00	ug/l	0.33	
TIC	3,282.50	mg/l	3,282.50	
TOC	10,475.00	mg/l	10,475.00	
COD	31,700.00	mg/l	31,700.00	
Total Suspended Solids	15,900.00	mg/l	15,900.00	
Total Dissolved Solids	318,000.00	mg/l	318,000.00	
Normality as NaOH	5.50	n		
Density	1.28	g/ml		



Table 6-26. Run 17, Tetrytol Explosive Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	0.7250	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	0.8280	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	106.0000	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	14.9000	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	0.1860	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	0.2770	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	0.4610	MAX			ug/m <sup>3</sup>
Acetaldehyde	11.6000	B	2.4300	B	ug/m <sup>3</sup>
Acetone	3,030.0000		16.0000	U	ppbv
Ammonia	73,300.0000		303,000.0000		ug/m <sup>3</sup>
Bromomethane	78.7000		41.3000		ppbv
Butanal	0.3600		0.0306	J	ug/m <sup>3</sup>
Carbon Dioxide	0.0200		0.0100		%
Carbon Monoxide	0.0000		0.0000		ppmv
Chloroform	58.2000		16.0000	U	ppbv
Crotonaldehyde	0.1180	J	0.0683	J	ug/m <sup>3</sup>
Cyanide	0.0003		0.0007		ug/m <sup>3</sup>
Cyclohexanone	0.7020	J	0.0264	JB	ug/m <sup>3</sup>
Ethylenimine			12,839.5000	J	ppbv
Formaldehyde	17.8000	B	11.2000	B	ug/m <sup>3</sup>
Heptanal	0.1410	J	0.0048	U	ug/m <sup>3</sup>
Hexanal	1.4700		0.1740	J	ug/m <sup>3</sup>
Methyl Chloride	25.2000	B	24.0000	U	ppbv
m-Tolualdehyde	0.7750		0.0057	U	ug/m <sup>3</sup>
Nitrous Oxide	1,403.0000		276.0000		ppmv
Nonanal	0.1460	J	0.0461	J	ug/m <sup>3</sup>
NOx	0.0000		2.1000		ppmv
Octanal	0.0873	J	0.0258	J	ug/m <sup>3</sup>
Oxygen	21.2000		20.8000		%
Pentanal	1.5400	B	0.0469	JB	ug/m <sup>3</sup>
Tetryl	21.8000	MAX			ug/m <sup>3</sup>
Total Hydrocarbons	540.0000		1,326.0000		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

#### 6.4.2 Discussion & Analysis:

1. The end of run liquid analyses indicates that the destruction rate efficiency achieved approximately 5 hours after cessation of the feeding of Tetrytol explosive to the reactor – 8 hours after the start of the run – ranged from 100.00% to 99.7847%. The TNT destruction rate efficiency for Runs 16 and 17 was 99.8982% and 99.8063% respectively. Picric Acid was detected during mid-run analysis as shown in Figures 6-31, 6-33 and 6-35, and in the end of run analyses for Runs 16 and 17.
2. The energetics loading for the three runs with Tetrytol is 5.0 – 5.5 weight-percent resulting in a total solids (dissolved and suspended) loading at the end of the run of between 21.3 to 33.3 weight-percent depending on the caustic strength.
3. The only “bad actor” detected in the hydrolysate is cyanide (possibly sodium cyanide) at a range of 259 to 705 ppm, increasing in concentration with increasing caustic strength. As stated in paragraph 6.1.2 above, the hydrolysis of energetics will produce cyanide and that the subsequent treatment of said hydrolysate using SCOW technology adequately reduces the hazardous compound concentrations in the hydrolysate feeds well below levels of concern. Picric acid was detected in the hydrolysate for Runs 16 and 17 at a level of 73 and 39 ppm. The Picric Acid in the hydrolysate is most likely showing up as sodium picrate because the likelihood of finding Picric Acid after more than 8 hours of processing is extremely low.
4. Trace amounts of HMX were detected in the hydrolysate for Runs 16 and 17, which is suspect since the HMX in the Composition B4 runs was 100% destroyed by the caustic. Consequently, it is unclear where the HMX is sourced from (unless it is a by-product from the nitration of Tetryl) and why it remains in the hydrolysate.
5. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. The off gassing fell-off quickly after the addition of the Tetrytol was completed (see Figures 6-32, 6-34, and 6-36), indicating that most of the reactions are taking place during energetic addition and progressing to completion in line with the liquid analysis data.
6. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
7. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. Foaming was not a problem with Tetrytol explosive.
8. Examination of the off-gas characterization for the three runs indicates that some energetic material (1,3,5-Trinitrobenzene, Dinitrotoluene, TNT, Tetryl) at low level were entrained in the gas stream during the addition phase of the process. TNT has a measurable vapor pressure at ambient, therefore one would expect TNT to come-off as part of the off-gassing stream. Also, the Tetrytol contained significant “fines” and dusting occurs as the Tetrytol falls into the reactor through the headspace air stream, possibly contributing to these readings. The energetic materials disappeared once the addition was stopped. Use of a condenser on top of the reactor to drop any entrained materials back into the reactor should be effective.

9. The major constituents of the off gassing were ammonia, acetone, bromomethane and nitrous oxide with ammonia dominating. These gasses can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release. The average range concentration of CO<sub>2</sub>, O<sub>2</sub>, CO, THC, NO<sub>x</sub> and N<sub>2</sub>O in the off gas stream during energetic addition for the three runs was: 0.0 - .02%, 21.1 – 21.4%, 0.0 – 3.0 ppmvd, 492 – 601 ppmvd, 0.0 – 2.8 ppmvd, 634 – 1,403 ppmvd, respectively and during digestion the concentration was: 0.0 - 0.01%, 20.8 – 21.2%, 0.0 ppmvd, 755 – 1326 ppmvd, 0.7 – 2.1 ppmvd, 86 – 276 ppmvd, respectively.
10. The inorganic materials (metals) detected in the hydrolysate end of runs analysis are sourced from the sodium hydroxide stock feed that contains some of these components.

## 6.5 M8 Sheet Propellant Hydrolysis Tests & Results (Runs 18, 19, & 20).

The objective of these tests is to clearly determine and define the optimum operating parameters for the M8 sheet propellant hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Pueblo Chemical Agent Disposal Facility for the destruction of propellant contained in the 4.2-inch Cartridge, Chemical Agent HT and HD, M2 and M2A1.

Mid-run liquid samples were not taken during the processing of the M8 propellant because of the configuration of the propellant charge. The M8 propellant is in multiple sheet form, sewn together with cotton threads. Separation of the sheet propellant from the cotton threads was impractical since the rubbery texture of the propellant gripped the threads. The dimensions of the bundles are as follows:

- L & W (maximum): 2.75-inches by 2.75-inches
- Number of sheets: up to 10
- Thickness (per sheet): 0.028-inches, -0.005-inches
- Hole Diameter: 1.31-inches, +0.10-inches

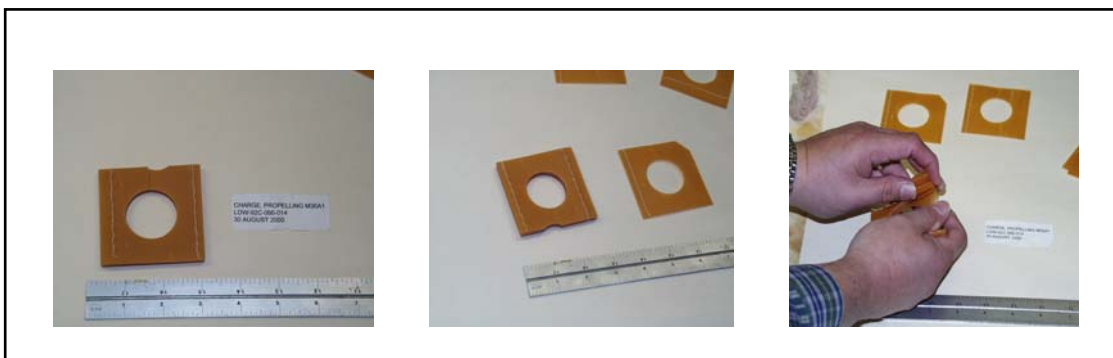


Figure 6-37. M8 Sheet Propellant

Therefore, the M8 propellant was manually fed in the “assembled” condition at the same as stated for the automatic feed rates when using the weigh-feeder system. Consequently, the operating and control parameters charts for the M8 propellant runs do not show the feed rate trace because the weigh-feeder system was not employed. As the sheet propellant was hydrolyzed, the freed cotton threads “blinded” the recirculation line inlet, thereby preventing liquid sampling from taking place during the run.

The table below identifies the process operating parameters for Runs 18, 19 and 20.

Table 6-27. M8 Propellant Test Parameters

Operating Condition	Run 18	Run 19	Run 20
M8 Feed Rate, lbs/hr			
1 <sup>st</sup> hour	50	50	50
2 <sup>nd</sup> hour	100	100	100
3 <sup>rd</sup> hour	150	150	150
4 <sup>th</sup> hour	200	200	200
Caustic Soda Concentration, wt%	12	21	26
Caustic Soda Feed, gal	700	700	700
Reactor Operating Temperature, °C	87	87	87
Agitation Speed, RPM	80	80	80
Date Conducted	4/3/2001	4/12/2001	4/18/2001

The following charts represent the process operating and control parameters for hydrolysis of M8 propellants:

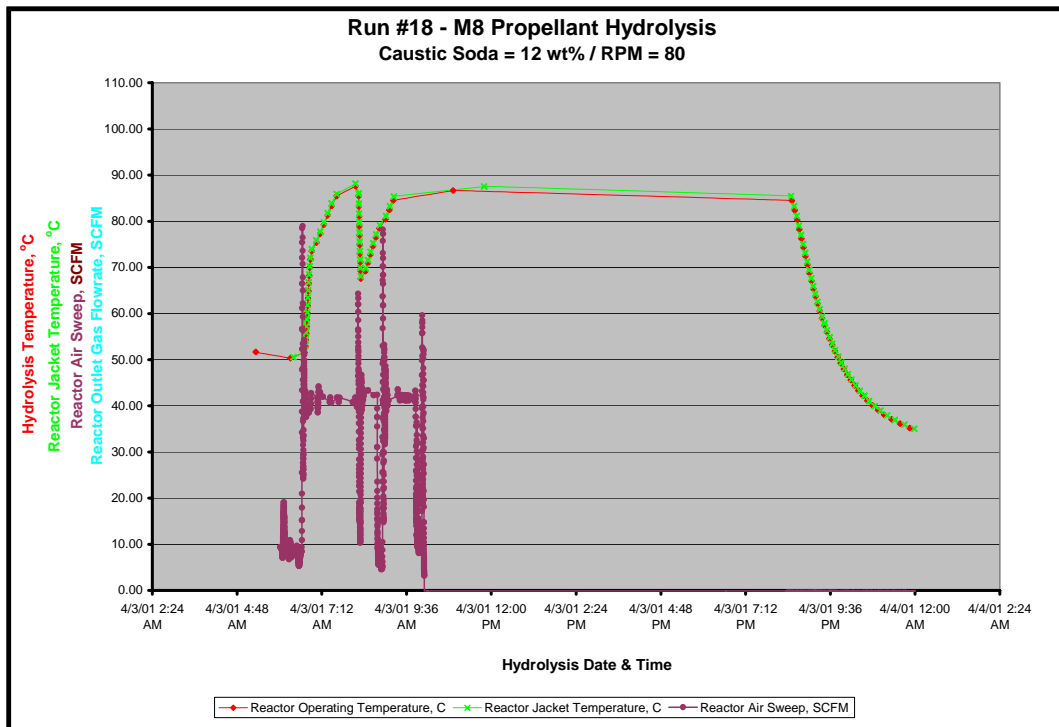


Figure 6-38. Run 18, Process Operating and Control Parameters

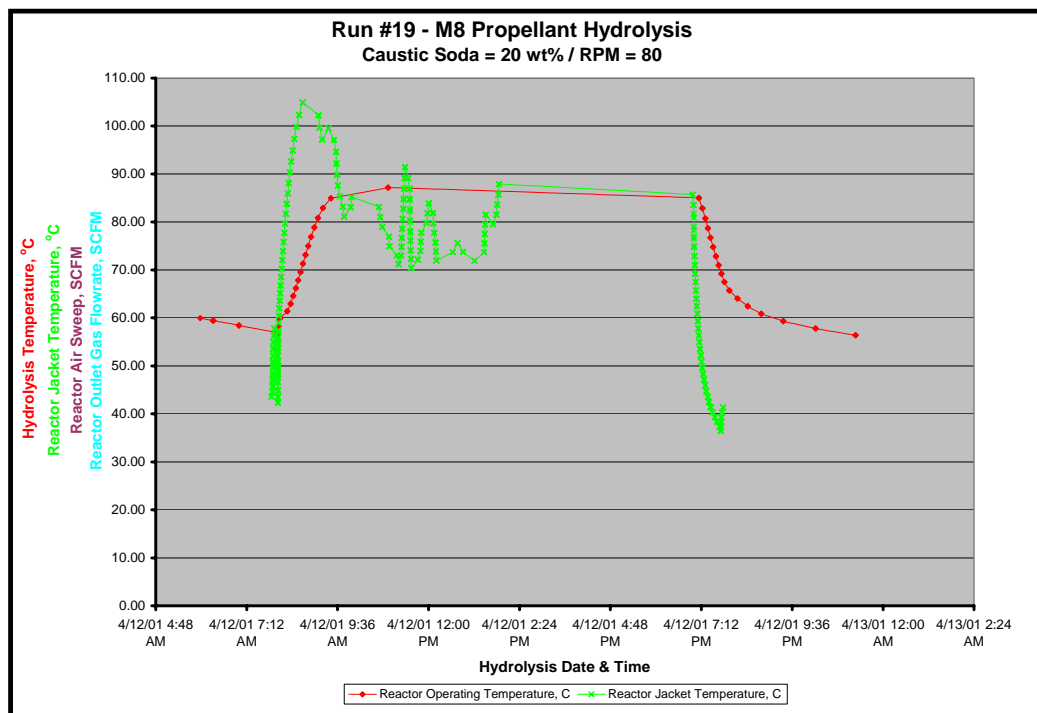


Figure 6-39. Run 19, Process Operating and Control Parameters

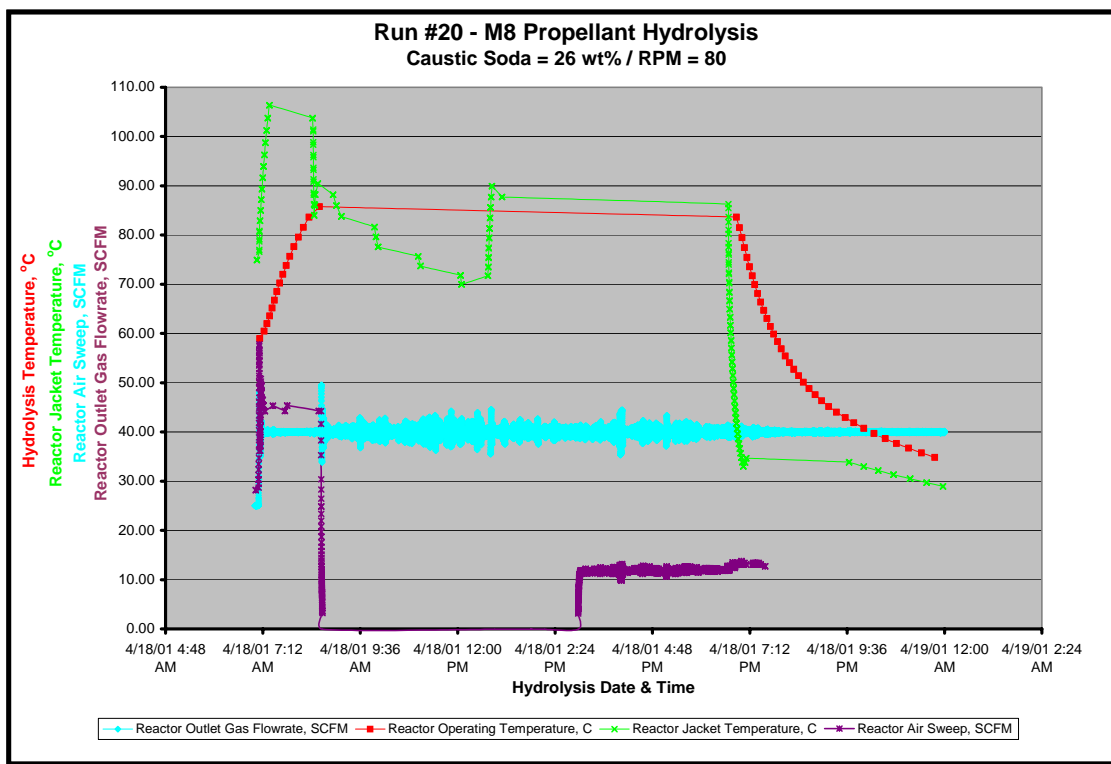


Figure 6-40. Run 20, Process Operating and Control Parameters

#### 6.5.1 Tests Results:

The following plots represent M8 propellant destruction as a function of reactor residence time.

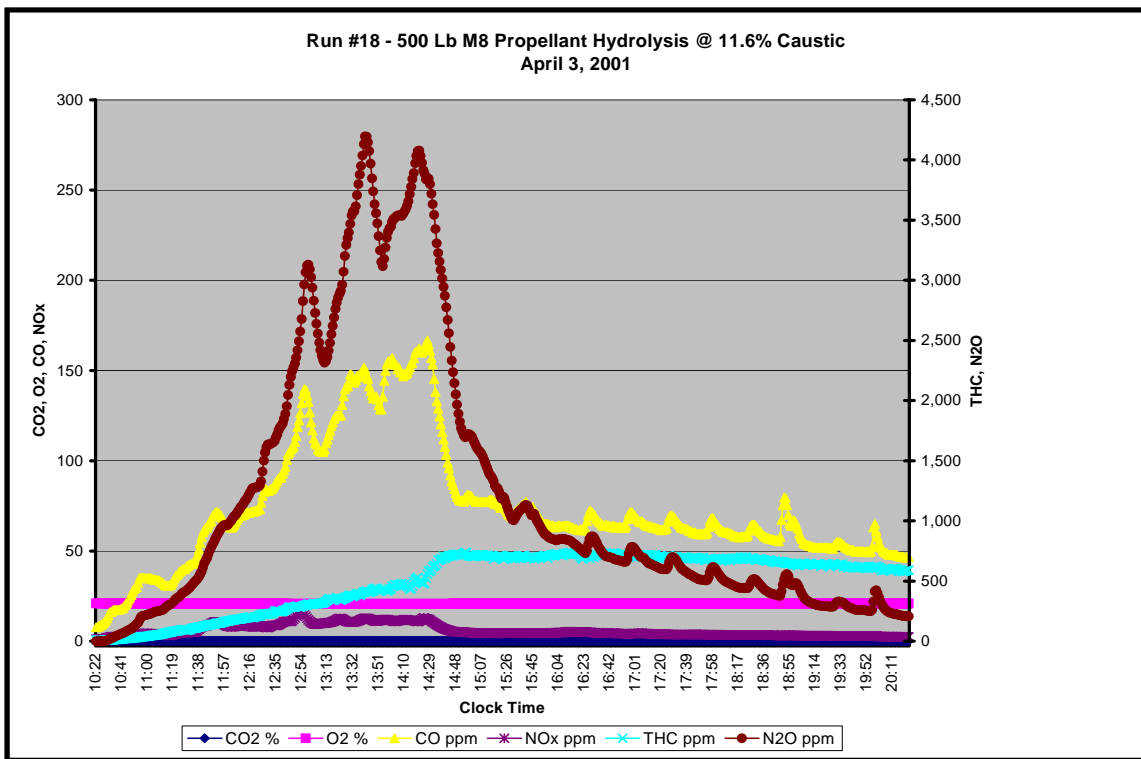


Figure 6-41. Run 18, Off-gas Production

Table 6-28. Run 18, M8 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
1,4:3,6-Dianhydro-.alpha.-d-glucopyranos	1,200.00	ug/l	1.20	J
2-Fluoro-4-nitrophenol	2,800.00	ug/l	2.80	J
Acetate	8,000.00	mg/l	8,000.00	
Aluminum	298.00	ug/l	0.30	
Ammonia	140.00	mg/l	140.00	
Barium	93.10	ug/l	0.09	
bis(2-Ethylhexyl)phthalate	4,300.00	ug/l	4.30	J
Calcium	51,000.00	ug/l	51.00	
Copper	2,100.00	ug/l	2.10	
Cyanide (Sodium Cyanide)	276,000.00	mg/l	276.00	
Fluoride	1,010.00	mg/l	1,010.00	
Formate	2,170.00	mg/l	2,170.00	
Magnesium	7,700.00	ug/l	7.70	
NG	11,199.00	ug/l	11.20	
Nitrate-N	2,560.00	mg/l	2,560.00	
Nitrite-N	6,090.00	mg/l	6,090.00	
Nitrocellulose	0.08	mg/l	0.08	J
Potassium	339,000.00	ug/l	339.00	
Sodium	50,620,000.00	ug/l	50,620.00	
Sulfate	120.00	mg/l	120.00	
Zinc	285.00	ug/l	0.29	
TIC	768.00	mg/l	768.00	
TOC	12,500.00	mg/l	12,500.00	
COD	15,000.00	mg/l	15,000.00	
Total Suspended Solids	132.00	mg/l	132.00	
Total Dissolved Solids	137,000.00	mg/l	137,000.00	
Normality as NaOH	1.29	n		
Density	1.10	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-29. Run 18, M8 Propellant Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
2-Butanone	361.00	U	2,220.00		ppbv
Acetaldehyde	6,260.00	D	9,400.00	D	ug/m <sup>3</sup>
Acetone	12,300.00		47,016.00		ppbv
Ammonia	575,000.00		1,850,000.00		ug/m <sup>3</sup>
Benzene	70.20		414.00		ppbv
Bromomethane	14.30	U	23.90		ppbv
Butanal	138.00		830.00		ug/m <sup>3</sup>
Carbon Dioxide	0.04		0.04		%
Carbon Monoxide	79.00		62.00		ppmv
Chloroform	10.70		18.00	U	ppbv
Crotonaldehyde	19.40		21.70		ug/m <sup>3</sup>
Cyanide	0.02		0.15		mg/m <sup>3</sup>
Cyclohexanone	29.30	B	18.30	B	ug/m <sup>3</sup>
Decanal	4.47	J	13.90		ug/m <sup>3</sup>
Ethanol			12,069.00	J	ppbv
Formaldehyde	282.00	B	246.00	B	ug/m <sup>3</sup>
Heptanal	3.38	J	8.69	J	ug/m <sup>3</sup>
Hexanal	36.30		29.70		ug/m <sup>3</sup>
Methylene Chloride	2,150.00	B	27.00	U	ppbv
NG	1,250.00				ug/m <sup>3</sup>
Nitrous Oxide	1,712.00		855.00		ppmv
Nonanal	43.00		5.29	J	ug/m <sup>3</sup>
NOx	7.30		3.10		ppmv
Octanal	3.81	J	7.37	J	ug/m <sup>3</sup>
Oxygen	21.10		21.10		%
Pentanal	26.00	B	46.30	B	ug/m <sup>3</sup>
Toluene	509.00		18.00	U	ppbv
Total Hydrocarbons	342.00		1,016.00		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank.



Table 6-30. Run 19, M8 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	10,000.00	mg/l	10,000.00	J
Ammonia	154.00	mg/l	154.00	
Barium	168.00	ug/l	0.17	
Calcium	30,800.00	ug/l	30.80	
Chromium	167.00	ug/l	0.17	
Cobalt	106.00	ug/l	0.11	
Cobalt	48.00	ug/l	0.05	
Copper	1,390.00	ug/l	1.39	
Cyanide (Sodium Cyanide)	378,000.00	ug/l	378.00	
Fluoride	622.00	mg/l	622.00	
Formate	3,050.00	mg/l	3,050.00	
Iron	4,410.00	ug/l	4.41	
Magnesium	7,420.00	ug/l	7.42	
Manganese	51.60	ug/l	0.05	
Molybdenum	33.60	ug/l	0.03	J <
NG	400.00	ug/l	0.40	
Nickel	189.00	ug/l	0.19	
Nitrate-N	2,390.00	mg/l	2,390.00	
Nitrite-N	5,840.00	mg/l	5,840.00	
o-Phosphate-P	368.00	mg/l	368.00	
Potassium	403,000.00	ug/l	403.00	
Sodium	72,680,000.00	ug/l	72,680.00	
Sulfate	274.00	mg/l	274.00	
Zinc	476.00	ug/l	0.48	
TIC	521.00	mg/l	521.00	
TOC	12,300.00	mg/l	12,300.00	
COD	32,700.00	mg/l	32,700.00	
Total Suspended Solids	364.00	mg/l	364.00	
Total Dissolved Solids	224,000.00	mg/l	224,000.00	
Normality as NaOH	3.20	n		
Density	1.19	g/ml		

J = Estimated Value; concentration is below limit of quantification

< = Concentration is below detection limit

Note: Off-gas production data was not collected for Run 19.

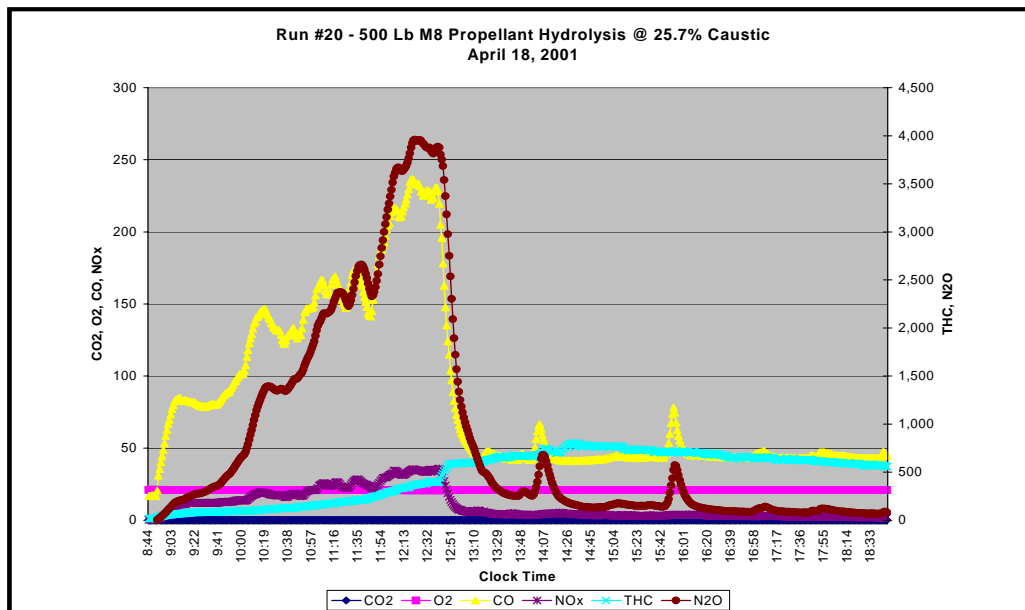


Figure 6-42. Run 20, Off-gas Production

Table 6-31. Run 20, M8 Propellant End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	4,320.00	mg/l	4,320.00	
Aluminum	265.00	ug/l	0.27	
Ammonia	74.50	mg/l	74.50	
Barium	78.20	ug/l	0.08	
Calcium	36,000.00	ug/l	36.00	
Chromium	148.00	ug/l	0.15	
Cobalt	48.00	ug/l	0.05	J
Copper	511.00	ug/l	0.51	
Cyanide (Sodium Cyanide)	133,000.00	ug/l	133.00	
Fluoride	291.00	mg/l	291.00	
Formate	1,380.00	mg/l	1,380.00	
Iron	1,800.00	ug/l	1.80	
Magnesium	18,200.00	ug/l	18.20	
Manganese	35.90	ug/l	0.04	
Molybdenum	33.60	ug/l	0.03	J
Nickel	216.00	ug/l	0.22	
Nitrate-N	675.00	mg/l	675.00	
Nitrite-N	1,580.00	mg/l	1,580.00	
o-Phosphate-P	100.00	mg/l	100.00	
Potassium	118,000.00	ug/l	118.00	
Sodium	34,550,000.00	ug/l	34,550.00	
Sulfate	74.50	mg/l	74.50	
Zinc	219.00	ug/l	0.22	
TIC	262.00	mg/l	262.00	
TOC	6,560.00	mg/l	6,560.00	
COD	14,900.00	mg/l	14,900.00	
Total Suspended Solids	348.00	mg/l	348.00	
Total Dissolved Solids	158,000.00	mg/l	158,000.00	
Normality as NaOH	2.60	n		
Density	1.14	g/ml		

J = Estimated Value; concentration is below limit of quantification

Table 6-32. Run 20, M8 Propellant Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
2-Butanone	439.00		642.00		ppbv
Acetaldehyde	7,780.00	D	8,180.00	D	ug/m <sup>3</sup>
Acetone	3,080.00		5,290.00		ppbv
Ammonia	425,000.00		1,830,000.00		ug/m <sup>3</sup>
Benzene	1,390.00		221.00		ppbv
Butanal	434.00		245.00		ug/m <sup>3</sup>
Carbon Dioxide	0.02		0.04		%
Carbon Monoxide	119.00		31.00		ppmv
Chloromethane	29.30		16.00		ppbv
Crotonaldehyde	39.90		18.90		ug/m <sup>3</sup>
Cyanide	0.07		0.05		mg/m <sup>3</sup>
Cyclohexanone	135.00		51.90		ug/m <sup>3</sup>
Decanal	13.80		5.33	J	ug/m <sup>3</sup>
Formaldehyde	336.00	B	204.00	B	ug/m <sup>3</sup>
Heptanal	24.80		8.73		ug/m <sup>3</sup>
Hexanal	69.90		38.90		ug/m <sup>3</sup>
Isopropyl Alcohol	24,968.10	J	129,625.60	J	ppbv
m-Tolualdehyde	348.00		263.00		ug/m <sup>3</sup>
NG	21,800.00				ug/m <sup>3</sup>
Nitrous Oxide	1,707.00		358.00		ppmv
Nonanal	35.30		6.99		ug/m <sup>3</sup>
NOx	18.10		2.90		ppmv
Octanal	15.00		8.09		ug/m <sup>3</sup>
Oxygen	21.20		21.20		%
Pentanal	81.50		16.00		ug/m <sup>3</sup>
Toluene	20.80		9.80		ppbv
Total Hydrocarbons	224.00		887.00		ppmv

J = Estimated Value; concentration is below limit of quantification.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank.

### 6.5.2 Cotton Threads:

At the conclusion of each run, the cotton threads from the M8 propellant bundles were wrapped around the lower agitator and shaft. The agglomeration of threads was removed from the shaft before the start of the next run. Also, threads adhering to the perforated recycle pipe were scrapped-off and removed from the reactor. Figure 6-43 below shows the threads that were removed from the reactor.



Figure 6-43. Recovered Cotton Threads from Hydrolysis of M8 Sheet Propellant Bundles

The cotton threads can present a problem to valves and pumps, and need to be addressed in the design of the full-scale facility.

### 6.5.3 Discussion & Analysis:

1. The end of run liquid analyses indicates that the destruction rate efficiency achieved approximately 5 hours after cessation of the feeding of M8 propellant to the reactor ranged from 99.9828% to 100.00%. The end of run analyses for Runs 18 and 19 indicated destruction rate efficiencies for NG of 99.9600 and 99.9985 respectively, which is surprising since NG is readily destroyed by caustic.
2. The only "bad actor" detected in the hydrolysate is cyanide (possibly sodium cyanide) at a range of 133 to 378 ppm. However, as stated in paragraph 6.1.2 above, the hydrolysis of energetics will produce cyanide and that the subsequent treatment of said hydrolysate using SCOW technology adequately reduces the hazardous compound concentrations in the hydrolysate feeds well below levels of concern.
3. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. The off gassing quickly fell-off after the addition of the propellant was completed (see Figures 6-41 and 6-42), indicating that the reaction was progressing to conclusion in line with the liquid analysis data. Unlike with M1 and M8 propellants, the THC level also dropped-off quickly after the addition of the M28 propellant was completed.
4. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
5. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. Foaming was not experienced with M8 propellant.
6. Examination of the off-gas characterization for the three runs indicates that NG vapor was in the gas stream only during the addition phase of the process. NG has a measurable vapor pressure at ambient, therefore one would expect NG to come-off as part of the off-gassing stream. Use of a condenser to drop any entrained materials back into the reactor should be effective; however, the condenser should be designed for potential service with NG vapors and cleaned accordingly when the system is decommissioned from service.
7. Other bad actors in the gas stream included low levels of benzene and toluene.
8. The major constituent of the off gassing was ammonia, which dominated the characterization. Other constituents at significantly lower levels were acetaldehyde, acetone, isopropyl alcohol and nitrous oxide. These gasses can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release.

## 6.6 M28 Leaded Propellant and Composition B4 Mixture Test & Result (Run 21).

The objective of these tests is to clearly determine and define the optimum operating parameters for the M28 leaded propellant mixed with Composition B4 explosive (86/14 wt%) hydrolysis process to support the design and installation of the full-scale hydrolysis process at the Blue Grass Chemical Agent Disposal Facility for the destruction of propellant and explosives contained in the 115mm Rocket and Rocket Warhead, Chemical Agent GB & VX, M55 and M56.

The table below identifies the process operating parameters for Run 21.

Table 6-33. M28 Propellant (Leaded) and Composition B4 Explosive Mix Test Parameters

Operating Condition	Run 21
M8 Feed Rate, lbs/hr	
1 <sup>st</sup> hour	50
2 <sup>nd</sup> hour	100
3 <sup>rd</sup> hour	150
4 <sup>th</sup> hour	200
Caustic Soda Concentration, wt%	20
Caustic Soda Feed, gal	700
Reactor Operating Temperature, °C	87
Agitation Speed, RPM	80
Date Conducted	4/19/2001

The following chart presents the process operating and control parameters for the hydrolysis for M28 Leaded Propellant / Composition B4 Explosive mixture:

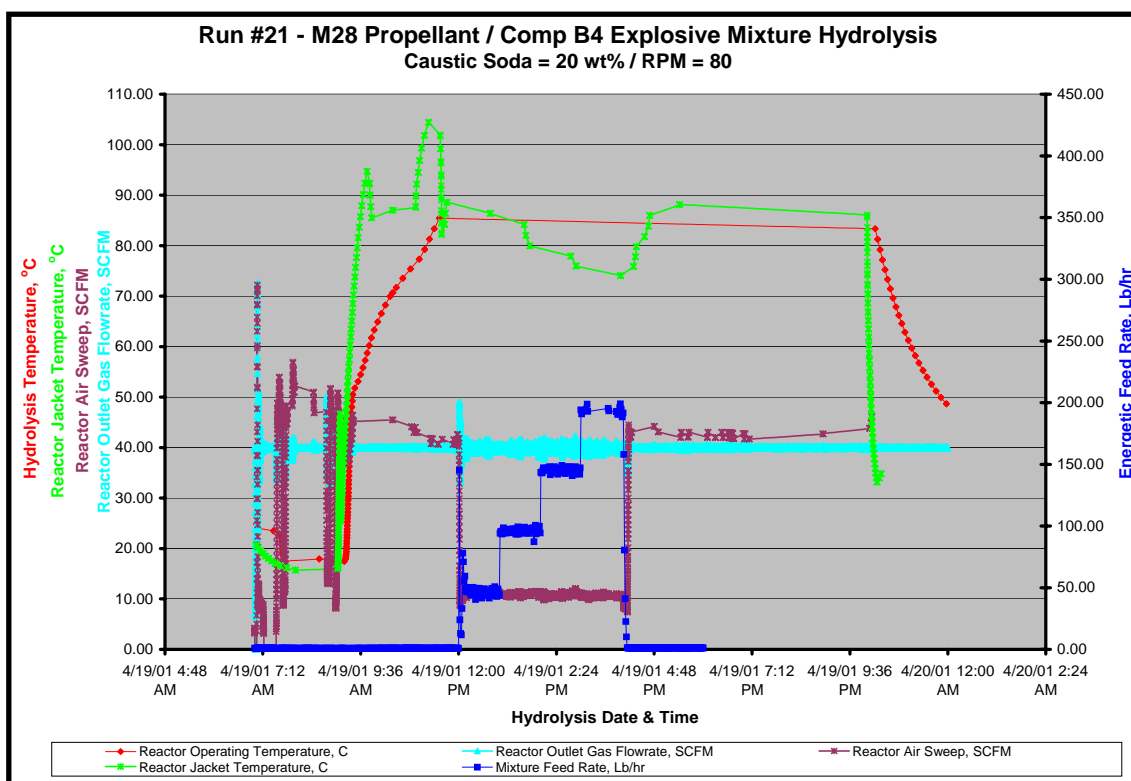


Figure 6-44. Run 21, Process Operating and Control Parameters

### 6.6.1 Tests Results:

The plots below represent the destruction of M28 leaded propellant and Composition B4 explosive mixture as a function of reactor residence time.

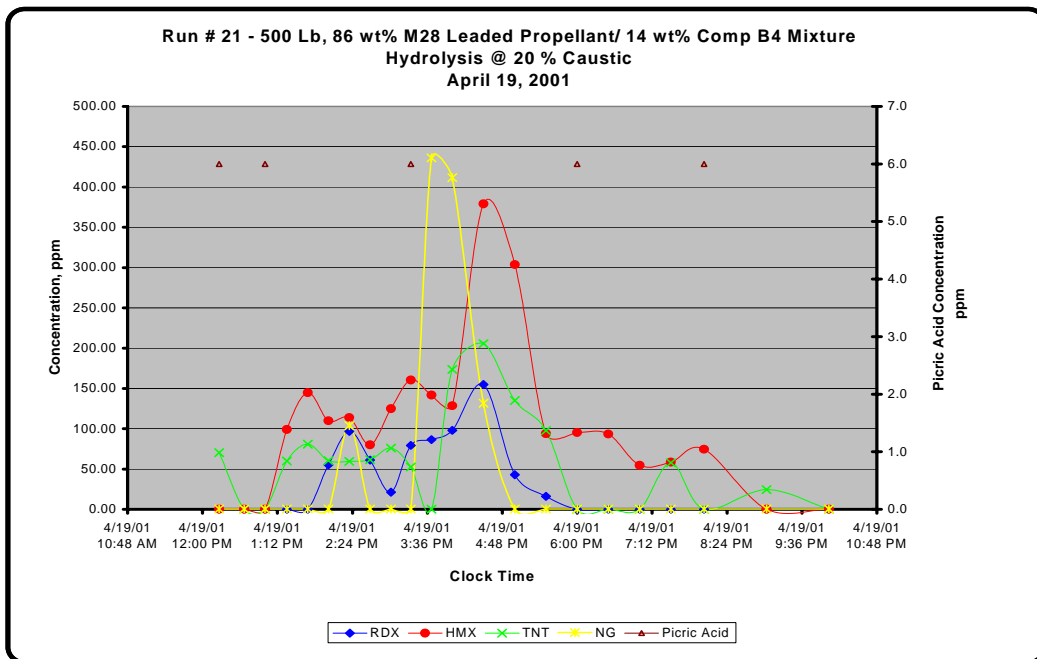


Figure 6-45. Run 21, Mid-Run M28 Propellant / Composition B4 Explosive Destruction Efficiency

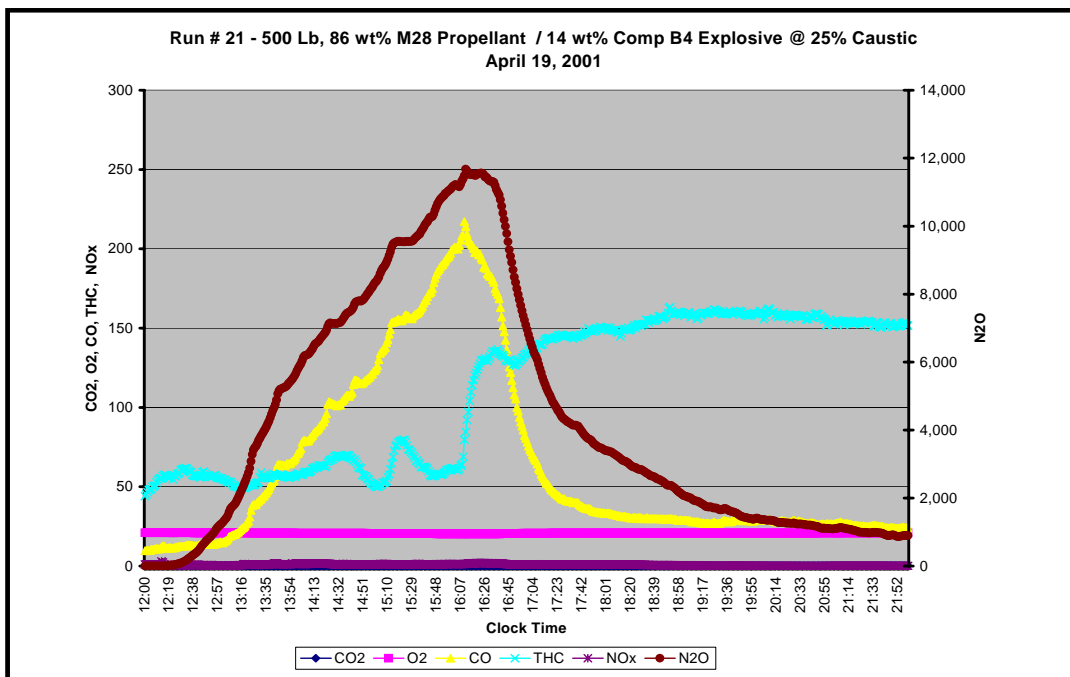


Figure 6-46. Run 21, Off-gas Production

Table 6-34. Run 21, M28 Propellant (Leaded) and Composition B4 Explosive End of Run Hydrolysate Characterization

End of Run Hydrolysate Analysis				
Component	Concentration	Unit	ppm	Note
Acetate	3,360.00	mg/l	3,360.00	
Aluminum	340.00	ug/l	0.34	
Ammonia	112.00	mg/l	112.00	
Barium	295.00	ug/l	0.295	
Calcium	35,900.00	ug/l	35.9	
Chromium	74.20	ug/l	0.0742	
Cobalt	22.30	ug/l	0.0223	J
Copper	297.00	ug/l	0.297	
Cyanide (Sodium Cyanide)	65,300.00	ug/l	65.3	
Di-n-butylphthalate	340.00	ug/l	0.34	J
Fluoride	230.00	mg/l	230.00	
Formate	1,240.00	mg/l	1,240.00	
HMX	24,180.00	ug/l	24.18	
Iron	1,110.00	ug/l	1.11	
Lead	79,300.00	ug/l	79.3	
Magnesium	9,740.00	ug/l	9.74	
Manganese	20.10	ug/l	0.0201	J
Molybdenum	36.70	ug/l	0.0367	J
Nitrate-N	472.00	mg/l	472.00	
Nitrite-N	1,310.00	mg/l	1,310.00	
Nitrocellulose	0.09	ug/l	0.00009	J
Phenol	390.00	ug/l	0.39	J
Potassium	4,540.00	ug/l	4.54	J
Sodium	25,030,000.00	ug/l	25030	
Sulfate	79.00	mg/l	79.00	
Zinc	119.00	ug/l	0.119	
TNT	29,790.00	ug/l	29.79	
TIC	140.50	mg/l	140.50	
TOC	4,547.25	mg/l	4,547.25	
COD	9,510.00	MG/L	9,510.00	
Total Dissolved Solids	66,500.00	mg/l	66,500.00	
Total Suspended Solids	330.00	mg/l	330.00	
Normality as NaOH	1.00	n		
Density	1.04	g/ml		

J = Estimated Value; concentration is below limit of quantification



Table 6-35. Run 21, M28 Propellant (Leaded) and Composition B4 Explosive Off-gas Characterization

Reactor Off Gas Analysis					
Component	During Energetic Addition	Note	During Reaction	Note	Unit
1,3,5-Trinitrobenzene	0.7250	MAX			ug/m <sup>3</sup>
1,3-Dinitrobenzene	0.8280	MAX			ug/m <sup>3</sup>
2,4,6-Trinitrotoluene	106.0000	MAX			ug/m <sup>3</sup>
2,4-Dinitrotoluene	14.9000	MAX			ug/m <sup>3</sup>
2,6-Dinitrotoluene	0.1860	MAX			ug/m <sup>3</sup>
2-Amino-4,6-Dinitrotoluene	0.2770	MAX			ug/m <sup>3</sup>
4-Amino-2,6-Dinitrotoluene	0.4610	MAX			ug/m <sup>3</sup>
Acetaldehyde	11.6000	B	2.4300	B	ug/m <sup>3</sup>
Acetone	3,030.0000		16.0000	U	ppbv
Ammonia	73,300.0000		303,000.0000		ug/m <sup>3</sup>
Bromomethane	78.7000		41.3000		ppbv
Butanal	0.3600		0.0306	J	ug/m <sup>3</sup>
Carbon Dioxide	0.0200		0.0100		%
Carbon Monoxide	0.0000		0.0000		ppmv
Chloroform	58.2000		16.0000	U	ppbv
Crotonaldehyde	0.1180	J	0.0683	J	ug/m <sup>3</sup>
Cyanide	0.0003		0.0007		ug/m <sup>3</sup>
Cyclohexanone	0.7020	J	0.0264	JB	ug/m <sup>3</sup>
Ethylenimine			12,839.5000	J	ppbv
Formaldehyde	17.8000	B	11.2000	B	ug/m <sup>3</sup>
Heptanal	0.1410	J	0.0048	U	ug/m <sup>3</sup>
Hexanal	1.4700		0.1740	J	ug/m <sup>3</sup>
Methyl Chloride	25.2000	B	24.0000	U	ppbv
m-Tolualdehyde	0.7750		0.0057	U	ug/m <sup>3</sup>
Nitrous Oxide	1,403.0000		276.0000		ppmv
Nonanal	0.1460	J	0.0461	J	ug/m <sup>3</sup>
NOx	0.0000		2.1000		ppmv
Octanal	0.0873	J	0.0258	J	ug/m <sup>3</sup>
Oxygen	21.2000		20.8000		%
Pentanal	1.5400	B	0.0469	JB	ug/m <sup>3</sup>
Tetryl	21.8000	MAX			ug/m <sup>3</sup>
Total Hydrocarbons	540.0000		1,326.0000		ppmv

J = Estimated Value; concentration is below limit of quantification.

MAX = Reported result was from a multi-fraction gas sampling train that contains both non-detected results and positive results.

U = Analyte was not detected.

D = Result obtained from analysis of a dilution or surrogate diluted below detection limit.

B = When applied to anions or organic analysis the qualifier indicates that the analyte was detected in the associated method/instrument blank

### 6.6.2 Neutralization:

This mixture was disposed of as hazardous waste because of the lead content in the M28 propellant formulation (~2 % lead stearate). Therefore, the pH was adjusted to ~10 using concentrated sulfuric acid (98+%), introducing the acid through the new spray nozzle at a slow rate and keeping the hydrolysate temperature at less than 50°C. The procedure worked satisfactorily although NO<sub>x</sub> emissions were again generated during the neutralization reaction.

### 6.6.3 Discussion & Analysis:

1. The end of run liquid analyses indicates that a 99.9172 % destruction rate efficiency was achieved approximately 6 hours after cessation of the feeding of M28 propellant / Composition B explosive mixture to the reactor – approximately 10 hours after the start of the run. HMX and RDX are detected in the hydrolysate, which was again surprising since both these energetics are readily destroyed by caustic. A low level of Picric acid was detected in the mid-run samples analysis as shown in Figure 6-45; however, Picric Acid was not detected in the end of run hydrolysate sample analysis.
2. The energetics loading for the M28 leaded propellant and Comp B explosive mixture is approximately 6.4 weight-percent resulting in a total solids (dissolved and suspended) loading at the end of the run approximately 7.7 weight-percent at 20 wt% caustic strength.
3. The only “bad actor” detected in the hydrolysate is cyanide (possibly sodium cyanide) at ~65 ppm and lead as Lead Hydroxide and/or Lead Picrate at ~79 ppm. As stated in paragraph 6.1.2 above, the hydrolysis of energetics will produce cyanide and that the subsequent treatment of said hydrolysate using SCOW technology will adequately reduce the hazardous compound concentrations in the hydrolysate feeds well below levels of concern. The lead is sourced from the lead stearate, which is 2% of the M28 propellant formulation. A low level of HMX and TNT (29.79 and 24.18 ppm respectively) remains at the end of run.
4. The airflow across of the reactor headspace was maintained at ~40 scfm during the test. The off-gassing quickly fell-off after the addition of the propellant was completed (see Figure 6-46), with the exception of THC<sub>s</sub>, indicating that the reaction was progressing to completion in line with the liquid analysis data. As previously stated, it is conjectured that the continued THC off-gassing was the result of dissolved gases and the continued reaction of the caustic solution with the by-products of the destruction of the NC chain (contributed by the M28 propellant).
5. The heat released by the exothermic reaction easily controlled by the reactor jacket cooling system, and the hydrolysate was maintained at the 87°C set point without difficulty.
6. The operating level in the reactor was maintained just above the lower impeller representing a starting volume of ~700-gallons. Foaming was not a problem with this mixture.
7. Examination of the off-gas characterization for the run indicates that some energetic materials (1,3,5-Trinitrobenzene, Dinitrotoluene, TNT and Tetryl) at low level were entrained in the gas stream during the addition phase of the process. TNT is to be expected since some dusting of the Composition B4 explosive will occur as the material fell into the reactor across the air stream. The Tetryl identification may have been residuals left in the traced Teflon gas sampling line back to the Instrumentation Van, or in the condenser system. The energetic materials disappeared once the addition was stopped. Use of a condenser to drop any entrained materials back into the reactor should be effective.

8. The major constituents of the off gassing were ammonia, acetone and nitrous oxide with ammonia dominating. These gasses can be effectively treated with a scrubber system, with the water from the scrubber then processed through the SCWO system as the final treatment step before release. The average concentration of CO<sub>2</sub>, O<sub>2</sub>, CO, THC, NO<sub>x</sub> and N<sub>2</sub>O in the off gas stream during energetic addition for this run was: 0.05%, 21.0%, 71 ppmvd, 86 ppmvd, 0.6 ppmvd, 5,385 ppmvd, respectively and during digestion the concentration was: 0.03%, 21.1%, 10 ppmvd, 211 ppmvd, 0.0 ppmvd, 895 ppmvd, respectively.

9. Lead Material Balance:

Lead Stearate comprised approximately 2% of the 430 pounds of M28 propellant used in the M28 propellant / Composition B explosive mixture test run, or approximately 8.6 pounds. The molecular weight (MW) of Lead Stearate is 774.15 and the MW of lead is 207.2. Therefore, the amount of Lead in the propellant is:

$$207.2 / 774.15 \text{ MW} \times 8.6 \text{ pounds} = \sim 2.302 \text{ pounds}$$

The Lead detected in the hydrolysate was 79.3 ppm, or equivalent to 79.3 mg/liter. The volume of the hydrolysate was approximately 800-gallons; therefore, the amount of Lead in the hydrolysate is:

$$79.3 \text{ mg/liter} \times 800\text{-gallons} \times 3.785 \text{ liters/gallon} = \sim 240120 \text{ mg or } \sim 0.53 \text{ pounds}$$

Consequently, ~ 78% of the Lead is unaccounted for, which is mostly likely to be found in the un-dissolved solids content of the hydrolysate in the form of lead hydroxide.

A second analysis performed on the hydrolysate to confirm the Lead level showed a 78.1 ppm concentration.

## 7.0 M1 PROPELLING CHARGE CONFIGURATION ISSUE -- CLOTH BAGS

The M1 propellant in the 105mm cartridges is configured in cloth bags for the purposes of zoning the round. The testing conducted under this program used loose M1 propellant since the M1 loaded propellant bags were not available in the stockpile. However, LANL was asked to conduct tests with the cloth bag material (spun viscose rayon, resin impregnated class 1, spec MIL-C-43157)) to determine if the cloth bag could be destroyed in the caustic solutions being used to hydrolyze the propellant; thereby saving downloading time (removal of the M1 propellant from the bag).



Figure 7-1. M1 Propellant Grains

## 7.1 Experiments with the Rayon Cloth.

Two sets of four swatches of rayon cloth were exposed to 6-, 12- and 20-weight percent NaOH at 93°C for 340 min. The swatches were photographed before and after the exposure to base. Mass loss of the swatches could not be determined due to a large amount of NaOH crystals adhering to the fibers when dried. Repeated rinsing of the swatches with water did not appear to improve the situation

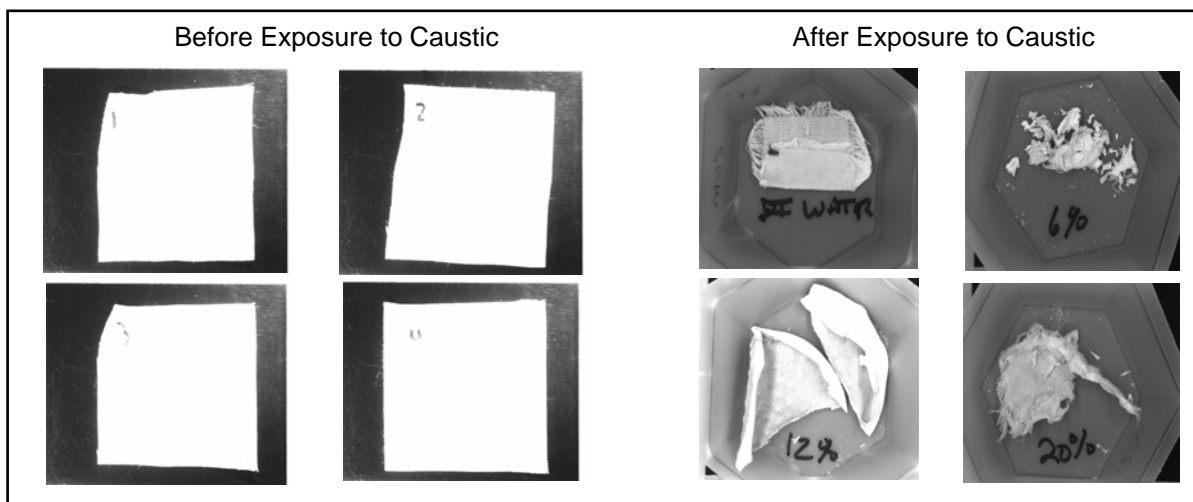


Figure 7-2. Rayon Cloth Samples

## 7.2 Recommendation.

The handling of the M1 propellant charges may present a problem. The rayon bag containing the M1 propellant was not digested during the testing conducted at LANL; however, it is conjectured that processing the rayon bag in caustic through an in-line homogenizer would most likely break-up the bag into small pieces that could then be effectively digested by the caustic solution. Bottom Line: The handling of the M1 propellant charges as a separate campaign should also address the handling of the rayon bag.

## 8.0 HYDROLYSATE PREPARATION FOR USE IN SCWO TEST AND EVALUATION PROGRAM

The PM decided late in the program to use the hydrolysates produced during the equipment commissioning and the test and evaluation program to support the continued testing of the Foster-Wheeler SCWO reactor at DPG. A defined hydrolysate specification did not exist. After much discussion, Foster-Wheeler provided the following recipe for hydrolysate: 9.2% energetic solids loading reacted with a 20% NaOH solution.

Since the hydrolysates were already produced, it was decided to execute the recipes in the laboratory at Holston AAP using Composition B explosive and M1 propellant individually so as to convert the proposed explosive loading into an actually measured solids loading. The results of that work are summarized below:

### 8.1 Composition B Explosive Hydrolysate.

#### 8.1.1 Laboratory Procedure:

1,000-grams of 20.19% caustic solution was prepared and charged to a standard (Holston AAP) 3-liter still. The caustic solution was heated to 87°C and 101.33-grams of Composition B was incrementally charged to the caustic solution over an approximate 5-minute period (representing the above stated recipe). The reaction mixture was held at 87°C ± 3°C for 6-hours. The hydrolysate was then cooled to 50°C, drained from the still into a Nalgene storage bottle and was allowed to sit overnight. The hydrolysate was filtered at 26°C through a coarse porosity glass crucible (approximate 20-micron pore size). Samples of the hydrolysate were taken to determine dissolved solids. 500-grams of the filtered hydrolysate was neutralized using 173.27-grams of 60.2% nitric acid. The neutralized hydrolysate was tested to determine suspended and dissolved solids.

#### 8.1.2 Laboratory Results – Solids Loading:

##### Composition B Hydrolysate:

- % NaOH 18.78% (average of 2 readings)
- Suspended Solids 0.25%
- Dissolved Solids 27.00% (average of three tests at 27.03%, 27.02%, and 26.96%)
- Total Solids 27.25%

##### Neutralized Composition B Hydrolysate:

- pH 8.3
- Suspended Solids 0.02%
- Dissolved Solids 29.17% (average of three tests at 29.20%, 29.18%, and 29.13%)
- Total Solids 29.19%

### 8.2 M1 Propellant Hydrolysate.

#### 8.2.1 Laboratory Procedure:

1,000-grams of 20.19% caustic solution was prepared and charged to a standard (Holston AAP) 3-liter still. The caustic solution was heated to 87°C and 101.33-grams of M1 propellant was incrementally charged to the caustic solution over an approximate 5-minute period (representing the above stated recipe). The reaction mixture was held at 87°C ± 3°C for 6-hours. The hydrolysate was then cooled to 50°C, drained from the still into a Nalgene storage bottle and was allowed to sit overnight. The hydrolysate was filtered at 26°C through a coarse porosity glass crucible (approximate 20 micron pore size). Samples of the hydrolysate were taken to determine dissolved solids. 500-grams of the filtered hydrolysate was neutralized using 176.69-grams 60.2% nitric acid. The solution was slightly acidic with an approximate pH = 6. Therefore, 9.98-grams of 20.19% NaOH was added to the mixture to increase the desired pH within the targeted range of 7 –10. The neutralized hydrolysate was tested to determine suspended and dissolved solids.

## 8.2.2 Laboratory Results – Solids Loading:

### M1 Hydrolysate:

- % NaOH 15.21% (average of 2 readings)
- Suspended Solids 0.29%
- Dissolved Solids 27.12% (average of three tests at 27.11%, 27.05%, and 27.19%)
- Total Solids 27.41%

### Neutralized M1 Hydrolysate:

- pH 9.8
- Suspended Solids 0.07%
- Dissolved Solids 30.73% (average of three tests at 31.04%, 30.50%, and 30.65%)
- Total Solids 30.80%

## 8.3 Particle Size.

Using the design documents for the Pueblo Chemical Agent Disposal Facility, General Atomics proposes to produce energetics hydrolysate at a rate of 400-700 lbs/hr, and cites a total of 5,000 gallons of storage tank capacity in the Energetics Rotary Hydrolyzer and the Hydrapulper before the hydrolysate is fed to SCWO. The hydrolysates will typically be held for 2.5 - 4.5 days before the hydrolysate is fed to the SCWO. Parsons cites similar flow rates with a 1,600-gallon energetics hydrolysate holding tank, so the energetics hydrolysate will typically be held for 1.5 days before the hydrolysate is fed to the 16,000-gallon ICB feed tank, where it is neutralized and diluted. Therefore, solids that may form after neutralization and storage on the order of weeks should not be relevant to the proposed processes.

## 8.4 Hydrolysate Prepared for DGP.

The hydrolysates stored in the tank farm were neutralized and shipped via tanker to DPG:

### Propellant Hydrolysate:

- Shipping Date: 8/16/01
- Trailer No.: 4231
- Weight (lbs): 40,680 lbs
- pH: 9.8
- % Solids (Total): 20.97% (average of six samples within a range of 20.85% - 21.05%)
- Batches: P-N-1, P-N-2, P-N-3, P-N-4
- HNO<sub>3</sub> (65%) Added: ~665 gallons

- Shipping Date: 8/23/01
- Trailer No.: 4853
- Weight (lbs): 42,660 lbs
- pH: 9.4
- % Solids (Total): 20.76% (Average of 6 Analyses)
- Batches: P-N-4, P-N-5, P-N-6, P-N-7
- HNO<sub>3</sub> (65%) Added: ~715 gallons

### Explosive Hydrolysate:

- Shipping Date: 8/17/01
- Trailer No.: 71404
- Weight (lbs): 43,840 lbs
- pH: 9.7
- % Solids (Total): 20.35% (average of six samples within a range of 20.28% -20.42%)
- Batches: E-N-1, E-N-2, E-N-3, E-N-4
- HNO<sub>3</sub> (65%) Added: ~767 gallons

- Shipping Date: 8/22/01
- Trailer No.: 11465
- Weight (lbs): 44,960 lbs
- pH: 9.8
- % Solids (Total): 21.13% (Average of 6 Analyses)
- Batches: E-N-5, E-N-6, E-N-7, E-N-8
- HNO<sub>3</sub> (65%) Added: ~764 gallons

The percent solids values provided are the total solids in the hydrolysate (suspended and dissolved).

#### 8.4.1 Filtering of the M8 Propellant Hydrolysate:

Before neutralizing the M8 propellant hydrolysate, which was stored separately from the M1 and M28 propellant hydrolysates, the cotton threads had to be filtered from the solution. This was performed using two in-line screen filters called Candle Filters. The dimensions of the overall filter were 44-inches long by 6-inches in diameter. The internal filter cartridge was 34-inches long by 3-inches in diameter. The internal filter essentially consisted of a 3-inch open pipe wrapped with a mesh screen connected to the pipe by stainless steel wire. The mesh size of the screen is 3/32 square inch mesh with 1/16 square inch actual opening size. The Figure 8-1 shows the threads that were removed from the hydrolysate.



Figure 8-1. In-line Screen Filters and Recovered Cotton Threads from M8 Propellant Sheet Bundles

Based on the amount of cotton threads recovered from the in-line screen filters, it would appear that the bulk of the cotton threads remained in the reactor (wrapped around the impeller blades) and were recovered from the reactor at the end of each run (see Figure 6-43).

#### 8.4.2 Neutralizing with Nitric Acid:

Foster-Wheeler, the contractor for the SCWO system that required the hydrolysates, requested that the hydrolysate be neutralized with  $\text{HNO}_3$  as opposed to  $\text{H}_2\text{SO}_4$ . The neutralization proceeded without problems, the  $\text{HNO}_3$  proved to be much “friendlier” than the  $\text{H}_2\text{SO}_4$  from a processing standpoint. The  $\text{H}_2\text{SO}_4$  (98%+) is hygroscopic, so much so that there is a significant heat release during dilution alone. The enthalpy of dilution, coupled with the enthalpy of neutralization is much, much greater than that for  $\text{HNO}_3$  (50-60% strength). This accounts for the significant temperature rise that was experienced during Run 1 neutralization using strong  $\text{H}_2\text{SO}_4$ .



## **9.0 EQUIPMENT / HARDWARE “LESSONS LEARNED”**

### **9.1 Acrison Loss-in-Weight Feeder.**

The performance of the Acrison loss-in-weight feeder was poor throughout the program. The major problem was during start-up of the feeder. The drive motor for the conditioning and feed auger repeatedly stopped because of a current overload at start-up. This problem is attributed to the design of the conditioning auger, which was modified before starting the M28 propellant tests. The modification appeared to solve the problem. Other problems included:

- The control system was not properly interfaced/designed for remote operation (i.e., operators were required to enter the processing building to reset frequent alarms).
- The control system would occasionally report an incorrect total mass greater than that loaded into the feed hopper (several percent higher).

The technical support from the vendor was also unsatisfactory. The vendor was reluctant to visit the work site to trouble shoot the problem, and when the problem was traced to the conditioning auger configuration, the modifications were executed by RONA. The aggressive program schedule contributed to problem of working with the vendor to resolve the feeder performance problems.

### **9.2 Recirculation Line.**

The performance of the recirculation line was marginal. The pump had difficulty pulling suction sufficient to initiate the recirculation flow at start-up. In addition, the direction of the flow, pulling from the top of the reactor and pumping into the bottom of the reactor, contributed to aeration. While this ensured that the discharge valve would not clog, it also impacted the performance of the mass flow meter, which is sensitive to aeration of the flow. This also impacted the performance of the liquid sampling system at times.

A preferred approach would be to design the reactor recirculation loop for bi-directional flows, (e.g., adding a second inlet/outlet port at the bottom of the reactor or a side port with the appropriate piping). The NRC and potential facility contractors asked, “Do we need the recirculation feature in the full-scale facility?” The recommendation is to include the recirculation loop for the flexibility it provides. The hardware and labor cost associated with installing this loop is insignificant compared to the total cost of the chemical weapons demilitarization facility.

### **9.3 Mass Flow Meter.**

The performance of the mass flow meter was unsatisfactory because the meter was installed before the suction inlet to the recirculation pump, cause aeration to occur, especially during the energetics addition stage of the process. Reinstalling the mass flow meter on the discharge side of the pump will solve the problem. There was not sufficient time in the schedule to reinstall the mass flow meter. From a facility standpoint, the mass flow meter is not essential to safe hydrolysis of energetics.

### **9.4 Agitator Shaft Seal.**

The use of water-seals for the reactor agitator, a requirement of RONA and the Holston AAP Safety Office, was proven to be a wrong choice. The recommended shaft seal is either a packing gland or a dynamic water-flushed graphite seal; both seals are readily available from equipment vendors as standard hardware. The potential for overflowing the reactor is probably a more serious concern than contamination of a seal.

### **9.5 Reactor Overflow Line.**

The over flow line from the reactor to the dump tank was installed at the wrong elevation. The overflow line should have been installed ~12-inches below the top of the reactor. This mistake caused the overflow line, a major fail-safe design element, to work improperly.

### **9.6 Sizing.**

The flow meters and valves for the acid and water lines were over sized by a considerable margin, which affected the ability to accurately measure flows at low rates. This was mostly of concern when introducing acid during the neutralization process, or trying to adjust pH of the hydrolysate by introducing additional caustic or water.

### **9.7 Commissioning Time Frame.**

Because of the aggressive schedule, the commissioning of the system was accelerated, resulting in problems later during the test program. Many changes that should have been made to improve the performance of the system had to be delayed or postponed indefinitely. However, the contractor as a necessary condition of operation to meet the schedule requirements accepted this.

### **9.8 Electrical / Instrumentation / Control.**

The following comment are germane to this program and should not be an issue for the implementation of a full-scale chemical weapons demilitarization facility:

- Designs for control systems are often done without consideration of maintenance, checkout, and startup activities. Provisions for devices to be electrically disconnected without shutting down an entire system are a requirement (e.g., fuses).
- PLC programmer not able to provide adequate support for the project time scale, largely because of time pressures but also because of lack of experience for energetic chemical processes. Required significant on-site support (expensive, time consuming).
- Rigidly structured, schedule driven programs do not allow flexibility for unknown situations and for routine abnormalities; an accepted cost of doing business for this program.
- Manual control of all field devices is a necessity for pilot plants as well as production facilities within the constraints of safety interlocks.

### **9.9 Positive Lessons Learned (Things That Worked Well!).**

- Redundant process monitoring equipment turned out to be very useful; e.g., measuring power consumption of recirculation pump, which allowed verification that hydrolysate was flowing in the recirculation line even when the mass flow meter displayed zero flow.
- Foaming can be effectively controlled using the level within the tank relative to the vortex formed by the agitator impeller, and the supplemental water spray (once the spray nozzle had been sized correctly).
- Modified Computer / PLC interface performed much better than might otherwise have been expected, and was worth the development effort.
- The reactor level sensor can detect foam.
- Manual overrides (e.g., temperature controls, valve controls) were vital to operating the hydrolysis system during the test program.
- PCS-7 style process monitoring (trends) can be exploited to learn more about the process.
- TRC feedbacks on reaction progress (the real time off-gas analyses) were a tremendous aid in tracking the progress of the reaction, especially during the commissioning runs.
- Modifying the liquid sampling system software for full programming of the sampling interval for the final few test runs simplified the duties of the control room operators.

## 10.0 CONCLUSIONS

The base hydrolysis, whether as individual energetic compositions or mixtures of energetics, is a proven process for the effective destruction of energetics recovered from the demilitarization of chemical weapons. The process is extremely robust, and provides a great deal of flexibility in terms of process rates, equipment selections and scaling.

The following responses are provided regarding the concerns cited by the NCR based on the bench-scale work performed by LANL and the pilot scale testing conducted at Holston AAP:

### 1. Destruction Rate Efficiency (DRE).

DREs ranged from a low of 99.7539 (Tetrytol) to 100.00% for all energetics processed. The tests performed on the hydrolysate show it to be safe to handle with the only intrinsic hazard being the high pH (13-14) of the final solution.

Several of the end of run analyses identified the presence of NG, HMX and RDX. This was surprising since these energetics are readily destroyed by caustic and/or had no clear source. It is possible that these unreacted materials may have been introduced from residuals in the sampling valve in the recycle line when the sample was drawn, biasing the results.

### 2. Optimum Processing Conditions.

Based on the energetics hydrolysis system testing performed at Holston AAP, it is concluded that the optimum processing conditions are: 20 weigh-percent sodium hydroxide, 87°C hydrolysate processing temperature, and 70-80 rpm agitator speed, and maximum 9-hour reactor resident time for propellants, explosives and mixtures. Using 25 weight-percent caustic had negligible effect on the reaction rate. Testing was performed with feed rates of 50-, 100-, 150- and 200-pounds per hour without difficulty. A feed rate of 500-pounds per hour was achieved during the commissioning trials with Composition B. Therefore, the hydrolysis process can safely process the energetic feed rates proposed for the Pueblo and Blue Grass Chemical Agent Disposal Facilities.

### 3. Characterization of Gas Generation.

The LANL bench-scale testing showed that the amount of gas produced during the hydrolysis of propellants was much less than that produced during the hydrolysis of Composition B4 or Tetrytol. Although all four major gas products ( $N_2$ ,  $N_2O$ ,  $NH_3$  and  $NO$ ) were detected, the quantity was minimal. A comparison between the rates at which gas is generated for the different energetics is depicted below:



The results of the full-scale testing conducted with the hydrolysis system correlates well with the LANL findings regarding gas generation and major gas products. Low levels of energetic materials (1,3,5-Trinitrobenzene, DNT, TNT, RDX, HMX, Tetryl, NG) are entrained in the off-gas stream during addition; however the energetics disappeared once the addition is completed. A condenser on top of the reactor and a water-mister will knock these materials back into the reactor. Cyanide, Benzene, Ammonia, Toluene, Xylenes, etc. that were detected in the off-gas stream can be effectively treated by a properly designed scrubber system.

#### **4. Energetic Residue.**

At the end of the test program, RONA personnel conducted a thorough inspection of the inside of the reactor to see if there are energetic materials coating the reactor. The following was observed:

- A crust like layer of energetic material was observed on the top of the reactor. This is attributed to commissioning Run 2 conducted at full capacity where foaming occurred. Most likely the foam carried with it energetic materials that coated inside the reactor.
- Upon inspection of the wall of the reactor within the working level, an insignificant layer of coating was observed and analyzed to determine its constituents. The result of this analysis is shown below: (awaiting results from RONA)

#### **5. Stack Off Gas Monitoring.**

The off gas leaving the scrubber in the stack was not monitored since this program was a pilot program and RONA was exempted from such monitoring. However, RONA did conduct visual monitoring and observed no unusual color or smell to the stack gas in the surrounding area.

#### **6. Rate of Reaction.**

LANL estimated the rates of reactions for the energetics in 12- and 20-weight percent caustic strength (see LANL Final Report). However, the particle sizes were not normalized; consequently, an absolute comparison cannot be made as to which material reacts the fastest and which material reacts the slowest. Based on work to date by LANL and with the pilot plant system, the slowest reacting energetics were the M1 and M8 propellants. The NC takes a long time to digest to its final by-products, as indicated by the sustained period of off gassing that occurred during the reaction. The Composition B/B4 and Tetrytol reacted very quickly with the reaction completed within 5-hours after the addition of energetics ceased. The M28 propellant reacted very quickly, more quickly than one would expect given its NC content. Some of this is attributed to the large percentage of NG, but another important element was the particle size of the surrogate M28 propellant (very small).

#### **7. Formation of Picric Acid.**

The formation of Picric Acid as a by-product of energetics hydrolysis is not a problem. Picric Acid was only detected at very low levels in the mid-run analyses for Tetrytol and was detected at a much lower level in the end of run analyses. This conclusion is supported by the bench-scale work performed by LANL that showed no Picric Acid present in the hydrolysate.

#### **8. Lead Material Balance (M28 Propellant).**

Approximately 22% of the lead introduced to the hydrolysis reaction as lead stearate in M28 propellant was accounted for in the hydrolysate (reported as ~79 ppm total Lead). The remaining lead is most likely in the suspended solids too low to account for the remaining (as lead hydroxide and/or lead picrate) analyzed at ~330 ppm. Further testing would be required to confirm this hypothesis.

## **9. Simultaneous Processing of Mixtures (Explosives and Propellants).**

A 500-pound mixture of M28 propellant (containing lead stearate) and Composition B explosive (86/14 weight-percentage ratio) was successfully process in the energetics hydrolysis system at Holston AAP. No problems were encountered. The DRE achieved was 99.999+ percent. The end of run analysis of the hydrolysate and the off-gas characterization tracked nicely with the analyses and characterizations obtained for the individual components. Processing this mixture, the most likely mixture to be encountered in the demilitarization of the chemical weapons, can be safely accomplished in the proposed Pueblo and Blue Grass Chemical Agent Disposal Facilities. This conclusion is supported by the bench-scale work performed by LANL.

## **10. Particle Size Reduction.**

The reactions involved in the hydrolysis of energetics are mass transfer limited, governed by the particle size of the materials present to the caustic solution (the smaller the particle size, the faster the rate of reaction). However, the explosives are all TNT based, and the TNT matrix quickly collapses at the operating temperature used during the test runs (87°C). Once the TNT melts (as well as reacts with the caustic), the particle size is controlled by material used in the formulation (RDX, HMX, and/or Tetryl). Particles sizes ranging from "fines" to chunks of Tetrytol approximately 1.25-inches in length and diameter were processed without difficulty. The propellant, specifically the M1 and M8, processed quickly and will not require any reduction. The M28 propellant is the only question mark -- how large will the particle sizes be when the M28 propellant is extracted form the rocket motor? The M28 propellant used in the testing was very small and not necessarily representative of the actual M28 propellant that will be seen by the production process. However, no problems are anticipated in processing ground M28 (grinding M28 propellant is being investigate at this time with Ecologic).

## **11. Cotton Threads and Rayon Bags.**

The handling cotton threads used to tie the M8 sheet propellant bundles must be addressed in the design of the energetic hydrolysis system. The rayon bags used to contain the M1 propellant should be emptied and then disposed of separately.

## **12. Solubility of Energetics.**

The aqueous concentrations of energetics is very low, even at high temperatures:

- RDX @ 90°C is ~300 ppm
- HMX @ 90°C is ~150 ppm
- TNT @ 60°C is ~675 ppm

Therefore, solubility is not a problem in designing the hydrolysis system for the proposed Pueblo and Blue Grass Chemical Agent Disposal Facilities

## **13. Heats of Reaction.**

LANL has provided an estimation of the heats of reactions for the various energetic compositions. These values can be used to calculate heat loading at various processing rate to assist in sizing the heat exchanger for the reactor jacket. However, developing heats of reaction for the by-products of the reaction represents a huge undertaking, and may not lend much value to the program.

#### **14. Foaming.**

Foaming was primarily controlled by adjusting the operating level of the hydrolysate within the reactor relative to the location of the vortex generated by the agitator blades. So long as a clearly defined vortex was maintained in the reactor, any foam formed during the hydrolysis would be quickly drawn below the surface and dissipated. Foaming was not experienced when processing propellants or the M28 propellant/Composition B explosive mixture.

#### **15. Tetryl Explosive.**

Tetryl explosive alone was not tested in the energetics hydrolysis system. Tetryl was not readily available from the inventory in the quantities required to test the system, and Tetryl presents handling problems (dusting) and is a health hazard. Furthermore, Tetryl is present in Tetrytol at 70+ percent. The testing with Tetrytol did not disclose any problems whatsoever processing the Tetryl constituent.

#### **16. Thermal Runaway.**

Based on work performed by LANL, the thermal runaway temperature for the propellants and explosives tested is 130°C or above for all base concentrations between (12 – 35 weight percent NaOH).

#### **17. Equipment Performance.**

The energetics hydrolysis reactor and supporting equipment performed acceptably during the test runs. While there were improvement identified that would have improved the operations during the test program, the aggressive schedule prevented most of these improvement from being implemented. However, for the most part the improvements were directed at improved data collection and experimentation, as opposed to correcting operating deficiencies, of which the only major problem was the loss-in-weight feeder that is not applicable to the proposed Pueblo and Blue Grass Chemical Agent Disposal Facilities. Of note, the system at Holston AAP was based on a 2000-gallon reactor. A smaller reactor, in the order of 500- to 1000-gallons volume, would be better suited for the proposed throughputs cited for the two facilities, based on the operational scenario chosen (batch versus semi-continuous operation).

#### **18. Equipment/System Maintenance.**

Over 300-hours of operating time were placed on the energetic hydrolysis system during the execution of the program. No major equipment failures were encountered during operations. The equipment used in the system is standard chemical processing hardware with extremely high degrees of reliability.

At the conclusion of the test runs, a Pfaudler representative visited Holston AAP to assess wear of the Glasteel® liner. Based on the manufacturing cards for the reactor, between 1-2 mils of glass was lost during the test runs on the bottom head of the vessel and about 3-feet up the side walls of the vessel, and similarly on the baffle, which is not very much. The glass was dull and rough to the touch, indicating that the "fire polish" was lost on this portion of the vessel. Loss of the polish indicates that the materials being processed are causing wear, but it in and of itself, is not going to accelerate wear. The only concern voiced by the Pfaudler, Inc. representative is that the roughen surface will tend to accumulate material and take more effort to clean, and the material accumulating on the Glasteel® will cause the continue corrosion. Pfaudler indicated that the usual approach by the user is to map the areas where some wear is occurring and monitor said area. When the Glasteel® thickness enters the 30-mil thickness is when closure scrutiny is required -- we are not close to that at this time. Bottom Line: The wear to date was not serious in the sense that the reactor was being compromised near term.

The Hastelloy C-276 agitator exhibited no wear whatsoever.

## REFERENCES

## REFERENCES

1. Bishop, R. and Sanchez, J., "Alkaline Hydrolysis of Composition B, Tetrytol, M1, M8, and M28 Propellant." Los Alamos Unclassified Report, LA-UR-01-4424, Los Alamos National Laboratory, Los Alamos, NM, 2001.
2. Bishop, R. and Sanchez, J., "Heat of Reaction for the Base Hydrolysis of Composition B, Tetrytol, M1, M8, and M28 Propellant." Los Alamos Unclassified Report, LA-UR-01-4425, Los Alamos National Laboratory, Los Alamos, NM, 2001.
3. "Manufacture of M28 Surrogate Propellant & Hydrolysates," Statement of Work, Radford Army Ammunition Plant, Radford, VA, October 1998.
4. Williams, Malcolm and Lemon, Earl, "Demilitarization of M28 Propellant," Alliant Techsystems, Inc. Incident Report, Radford Army Ammunition Plant, Radford, VA, October 2000.
5. Pfaudler Reactor Specifications and Requirements, Pfaudler, Inc. Rochester, NY, September 2000.
6. Wilson, Andrew; Hammonds, Jerry; and Plum, Gail, "Standard Operating Procedures for Hydrolysate Pilot Plant, Building G-10," Royal Ordnance North America, Inc. (Ordnance Systems, Inc), Holston Army Ammunition Plant, December 2000.
7. Wilson, A. R.; Ervin, M. J.; Barnett, L.; and Pierson, J., "Holston Army Ammunition Plant Building G-10 Energetics Material Hydrolysis Facility Failure Mode Evaluation Report (Initial)," Royal Ordnance North America, Inc. (Ordnance Systems, Inc.), Holston Army Ammunition Plant.
8. Wilson, A. R.; Ervin, M. J.; Barnett, L.; and Pierson, J., "Holston Army Ammunition Plant Building G-10 Energetic Material Hydrolysis Facility Failure Mode Evaluation Report (Final)," Royal Ordnance North America, Inc. (Ordnance Systems, Inc.), Holston Army Ammunition Plant.
9. System Installation Drawings, Holston Army Ammunition Plant Building G-10 Energetic Material Hydrolysis Facility, Royal Ordnance North America, Inc. (Ordnance Systems, Inc.), Holston Army Ammunition Plant, December 2000.
10. Belcher, Luther, "Cyclotol and Tetrytol Hydrolysis Operations at Pantex Plant," Mason & Hanger, Corp., Amarilo, TX, November 2000.
11. "Test Plan Requirements (TPR), Characterization of an Energetic Hydrolysis Reactor System at Holston Army Ammunition Plant/BAE Systems," U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ, June 2001.





APPENDIX A  
ACRONYMS AND ABBREVIATIONS



ACWA	Assembled Chemical Weapons Assessment
AAD	Army Ammunition Depot
AAP	Army Ammunition Plant
ARDEC	Armament Research, Development and Engineering Center
°C	degrees Centigrade
CW	Chemical Weapons
DPG	Dugway Proving Ground
DRE	Destruction Rate Efficiency
EST	Engineering Scale Test
EDP	Engineering Design Package
°F	degrees Fahrenheit
ft <sup>2</sup>	square foot
FMEA	Failure Mode and Effects Analysis
FY	Fiscal Year
gal	gallon
g/l	grams per liter
HDPE	High Density Polyethylene
HSAAP	Holston Army Ammunition Plant
kJ/g	Kilo-joules per gram
LANL	Los Alamos National Laboratory
lbs/hr	pounds per hour
mg/l	milligrams per liter
ml	milliliter
NLT	No Later Than
NRC	National Research Council
NSWC	Naval Surface Weapons Center
PM	Program Manager
ppbv	parts per billion by volume
ppm	parts per million
ppmvd	parts per million volume density
RONA	Royal Ordnance North America
rpm	revolutions per minute
scc/g	standard cubic centimeter per gram
scfm	standard cubic feet per minute
SCWO	Super Critical Water Oxidation
SET	Solvated Electron Technology
SOP	Standard operating Procedure
TACOM	Tank-Automotive and Armaments Command
TOC	Total Organic Compounds
TPR	Test Plan Requirements
ug/l	micrograms per liter
ug/m <sup>3</sup>	micrograms per cubic meter
VOC	Volatile Organic Solvents
wt%	weight percent



APPENDIX B  
NRC CONCERNS



## Characterization & Optimization Responding to the NRC Concerns

The following issues/concerns identified by the National Research Council (NRC) will be addressed during the Phase I design activities, and the test programs conducted during the Phase II and optional Phase III efforts.

1. Determine the particle size reduction of the energetic that must be achieved for proper operation:

There are two issues associated with particle size:

- The particle size of the incoming energetics and its impact on the hydrolysis process
- The resulting particle size of the salts from the hydrolysis

Particle size of incoming energetics: As part of Phase 1, a bench-scale study will be initiated to determine the effect particle size has on the hydrolysis process. In addition, methodology will be investigated for handling the incoming energetics including the particle size of the energetics and final recommendations presented to PM ACWA. However, it may be difficult to reduce the size of energetic before introduction to the hydrolysis reactor by size reduction equipment because of safety considerations. Since reaction of the energetic with caustic will happen regardless of the particle size of the energetics, this office feels that it would be better to increase the alkaline concentration to assure completion of the hydrolysis. However, some work performed by Los Alamos National Laboratory (LANL) has indicated that there is a limit to this approach. If this approach is unsuccessful, then studies aimed at increasing the residence time or increasing the rate of agitation will be conducted.

Resulting particle size of the salts from the hydrolysis: Phase II will investigate optimizing particle size of the finished product through control of the reactor operating parameters. A determination will be made if some type of re-sizing equipment, such as a homogenizer, will be needed for the finished product (hydrolysate) stream. In this case, a homogenizer may be used in a reactor recycle loop as a means to simultaneously reduce the particle size of residual unreacted energetics and to increase the effective residence time.

2. Determine the solubility of energetic in specific alkaline solutions:

Naval Surface Weapons Center (NSWC) and Los Alamos National Laboratory (LANL) will collaborate on solubility studies based on their extensive experience with the hydrolysis process chemistry. LANL will also review the present database on hydrolysis of energetic materials. Based on the LANL work, the solubility of these materials in alkaline solutions and an approach to prevent emulsification of the energetics will be developed and verified during the Phase II effort. Samples will be taken from the pilot plant during the trial runs of Phase II to determine solubility levels, and to assure that the method of hydrolysis chosen has resolved this problem.

3. Establish the process design of the unit operations and identification of the processing parameters:

During Phase II, trial runs will be conducted at different residence times, feed rates, temperatures, pH, and agitation levels to optimize the hydrolysis process parameters and produce an acceptable final product. Samples of the hydrolysate will be collected to identify the products as a function of these optimized process parameters. During these runs, the following processing parameters will be refined:

- Determine the critical temperature for conducting the hydrolysis reaction based on efficiency (time of reaction, residence time, completeness of reaction and products produced). Operating temperature should not exceed 150 C for any energetic to avoid detonation.
- Quantify the amount of heat that must be absorbed during the exothermic reaction. Operating at a 20% caustic strength is being considered to ensure completeness of reaction and reduce the residence time within the reactor. However, this will also put an additional demand on the cooling system for the reactor jacket.
- Determine the optimum rate for the addition of the energetics to the reactor. This is considered a critical parameter since it will determine the amount of heat liberated by the exothermic reactions as a function of time, and will also impact the thoroughness of the reaction, the demands on the agitation, and the possible formation of undesirable products.
- Establish the effective working volume for the reactor. If foaming occurs, or if there are volatiles, we need to ensure that the liquid/solid level in the reactor is not so high as to promote volatiles/solids from being driven off and into the air handling system.
- If required, determine the actions that must be taken to address the foaming associated with wax containing formulations; e.g., use of surfactants will be investigated to keep the wax fully dispersed in the hydrolysate mix.
- From a safety standpoint, develop a contingency plan to respond to a sudden shut down of the system. The concern is that the shutdown occurs during the early phase of the hydrolysis reaction when heat generation is at a maximum. Once there is a system shut down there is a need to know what's inside the reactor to make sure that it is safe to clean.

4. Characterization of the actual products (and by-products; i.e., formation of undesirable products during the hydrolysis process) as a function of the extent of reaction:

During the optimization of the process parameters in Phase II, samples will be taken to determine the products and by-products. This information will be used to optimize the hydrolysis process and to eliminate the formation of undesired products. Specifically:

- Products produced by the hydrolysis reactions will be fully characterize as a function of time to understand the reactions that are taking place during hydrolysis
- Picric Acid: The NRC has identified the formation of picric acid as a concern. Picric acid is formed from the degradation of tetryl at elevated temperature. Consequently, the potential of picric acid to be formed is always present if the hydrolysis reaction is incomplete and the environmental conditions are at elevated temperature.
- Stability of the hydrolysate: Continuation of the reactions after the hydrolysis of the energetics is completed is a concern of LANL, PANTEX and NSWC and needs to be addressed/understanding. The hydrolysate solution must be relatively stable and capable of being held for post-treatment processing. If the hydrolysate solution is not stable and reactions continue to occur, a release valve with a gas scrubber system should be investigated to insure there are no gas build up in the storage vessel.
- Final processing of the hydrolysate: Characterizing the hydrolysate for the next processing step is important. PANTEX noted significant solids in the hydrolysate. And, Pine Bluff Arsenal's SCWO for instance, can not inject slurries with particle sizes in excess of 100 microns.



In addition, as recommended by the NRC, whatever unit operations follows hydrolysis will be designed to accept emulsified nitro aromatic compounds

5. Selection of chemical sensors and process control strategies to ensure those unit operations following hydrolysis can accept the product of hydrolysis:

The chemical sensors and process control strategies will be developed during Phase I and evaluated during Phase II. After determination of all products and by products in Phase II, sensors and process control strategies will be refined and supplemented as necessary.

Phase III (optional) will be used to prove-out additional controls and control strategies for the supporting operations, if required by the PM.

6. Development of a preventive maintenance (PM) program that minimizes the possibility of incidents during cleanups of accumulated precipitates:

The kinetics study in Phase I will be used to assist in eliminating or minimizing the formation of undesirable products. Undesirable products could cause maintenance problems. The rate of build-up (or generation rate) of by-product salts that are potentially energetic will be assessed during testing, and a PM will be developed to prevent unnecessary operating conditions that may jeopardize worker safety. Trial runs will be performed during Phase II to determine the type of maintenance needed and the frequency. Material of construction will be investigated and chosen so that the material selected will resist alkaline, acid solutions, products and by-products of the hydrolysis.

7. Finding: The conditions under which aromatic nitro-compounds, such as TNT or picric acid, will emulsify in the aqueous phase and not be completely hydrolyzed are not well understood. Therefore, this type of material could be present in the output stream from an energetic hydrolysis:

This will be studied during Phase I. In addition, the final product produced during Phase II will be analyzed for the presence of aromatic nitro compounds. If these compounds are detected, a plan will be formulated as to the best way to eliminate (or minimize) this by-product. Removal of these compounds from the final product (hydrolysate), if necessary, will be investigated in Phase III.

8. Finding: The products of hydrolysis of some energetic materials have not been characterized well enough to support simultaneous hydrolysis of different kinds of energetic material in the same batch reactor.

As part of Phase I, the feasibility of simultaneous hydrolysis of different energetic materials in the same batch this will be investigated. However, safety issues may make this an unacceptable scenario. In addition and as recommended by the NRC, this program will investigate the formation of picrates from the hydrolysis of nitro aromatic compounds to assure they will not combined with M28 propellant.



APPENDIX C  
OFF GASSING ANALYTICAL PROCEDURES



PM ACWA ENERGETIC HYDROLYSATE PRODUCTION  
HOLSTON AAP SITE  
GAS SAMPLING OVERVIEW

TRC's role on the PMACWA Energetic Hydrolysate program being conducted at the Holston Army Ammunition Plant is to quantify the gaseous components being released from the hydrolyzation process. In order to accomplish this goal, an integrated gas sample is withdrawn from the 01 position (or the exhaust vent) of the Reactor Vessel and transported to the on-site analytical laboratory operated by TRC. Two types of samples are then collected in that laboratory: 1) Near real-time sampling of gaseous components that are conducive to analysis by Continuous Emission Monitoring System (CEMS); and, 2) Batch samples that are collected using an adsorption media or absorbing solution that are recovered and sent to an off-site laboratory for final quantification. The CEMS analyzers provide minute-minute trends of the concentrations of the individual gaseous compounds while the batch trains yield one value that represents an average concentration for the entire test run. Table 1 details the individual test methods that TRC is using in support of the PMACWA test program.

*Table 1. Test Methods*

<i>Parameter</i>	<i>Method</i>	<i>Abbreviation</i>	<i>Media Type</i>	<i>Laboratory</i>
Oxygen/Carbon Dioxide	EPA Method 3A	O <sub>2</sub> /CO <sub>2</sub>	CEMS	On-site
Moisture	EPA Method 4	Bws	Gravimetric	On-site
Nitrogen Oxides	EPA Method 7E	NO <sub>x</sub>	CEMS	On-site
Carbon Monoxide	EPA Method 10	CO	CEMS	On-site
Total Hydrocarbons	EPA Method 25A	THC	CEMS	On-site
Aldehyde/ketones	SW-846 Method 0011	Ald/Ket	DNPH	DAT, Inc.
Ammonia/Hydrogen Cyanide	EPA CTM 027/M26A	NH <sub>3</sub> /HCN	H <sub>2</sub> SO <sub>4</sub> /NaOH	Philip Analytical
Energetic Materials	CHPPM STEM	STEM	Imp/XAD	CHPPM
Volatile Compounds	EPA TO-15	TO-15	SUMMA	Philip Analytical
Nitrous Oxide	NIOSH 6600	N <sub>2</sub> O	IR	On-site by Miran 1B2

The sampling apparatus is divided into the following functional groups or systems in order to collect these samples. The following items are described in the direction of the sample gas flow (from Reactor Vessel to the analytical collection system maintained in the trailer):

1. A 1-inch ID Teflon® sample probe is positioned in the gas stream at the exhaust vent of the Reactor Vessel immediately exit of the headspace of the vessel. This probe is connected to three separate Teflon® sample lines approximately 350 feet in length. The lines are steam traced inside the building (about 150 feet) and electrically traced once they exit the restricted area of the building (about 200 feet) and are maintained at approximately 225-250 °F in order to prevent condensation of moisture (or organic compounds) during transport. The three lines have the following function:

*Line 1 - The Batch Train sample line* – is a 0.5-inch ID Teflon sample line that is used to transport approximately 20 Liters/min of headspace gas to the individual batch trains.

*Line 2 – The CEMS Sample line* – is a 0.375-inch ID Teflon sample line that is used to transport approximately 10-15 Liters/min of headspace gas to the CEMS analyzers.

*Line 3 – The CEMS Calibration line* – is a 0.375-inch ID Teflon sample line that is used to transport calibration gas from the mobile laboratory to the sample valve and back to the CEMS analyzers in order to calibrate the analytical instruments.

2. The CEMS portion of the gas sample is directed to the back of the analytical trailer and is divided once it enters the mobile laboratory as follows:

A small portion of the sample is maintained heated and is directed to the total hydrocarbon analyzer in order to analyze for total VOC content of the gas stream. It is important that this sample remains heated to prevent condensation of any organic species that may be present.

The bulk of the sample goes through a sample conditioning system that is designed to remove the moisture from the sample stream prior to analysis. The gas stream is then further split to the following analyzers for near real-time analysis and data collection: Oxygen (O<sub>2</sub>) Analyzer, Carbon Dioxide (CO<sub>2</sub>) Analyzer, Carbon Monoxide (CO) Analyzer, and the Nitrogen Oxides (NO<sub>x</sub> comprised of NO and NO<sub>2</sub>) Analyzer.

3. The output signal from each of the CEMS analyzers is recorded each second by the data acquisition system (DAS). From these data a 1-minute average is calculated and recorded by the DAS that can export the information to a Microsoft Excel file. Each analyzer is calibrated through the entire sample system before and after each test run using the calibration sample line. After the test run is completed the data are then corrected for calibration error or analyzer drift. The data are subjected to a series of quality assurance and quality control measures that are specified by the sampling methodology to verify the data is within precision and accuracy guidelines.

4. The Batch Train portion of the gas sample enters the front of the trailer and is directed to a multi-port Teflon® sample manifold that is maintained at approximately 250 °F. From that manifold the gas sample is split to the following sample trains:

*STEM Train* – The sampling train for energetic materials is a multi-impinger sample train maintained in chilled ice-bath followed by an adsorption media of XAD resin. The sample train is recovered on-site and sent to an off-site laboratory for analyses.

*Aldehyde/Ketone Train* – The sampling train for aldehyde/ketone compounds is a multi-impinger sample train filled with an absorbing solution containing a derivitizing agent maintained in a chilled ice-bath. The sample train is recovered on-site and sent to an off-site laboratory for analyses.

*Ammonia/Hydrogen Cyanide Train* – The sampling train for ammonia (NH<sub>3</sub>) and hydrogen cyanide (HCN) is a multi-impinger sample train filled with an absorbing solution maintained in a chilled ice-bath. The sample train is recovered on-site and sent to an off-site laboratory for analyses.

*VOCs* – An evacuated SUMMA canister is used to collect an integrated sample over the test period to be analyzed for a specific set of volatile organic compounds. The sample is sealed and sent to an off-site laboratory for analyses.

*Nitrous Oxide* – An integrated sample is withdrawn from the sample manifold and directed to a continuous analyzer to measure the N<sub>2</sub>O concentration. The N<sub>2</sub>O is measured real time and the data is logged into the DAS described in Item 3. This analyzer is operated from the Batch Train manifold rather than the CEMS because it requires a fairly large volume of sample gas.

5. The individual sample trains are transported to the Recovery Area at the conclusion of the sample run. Each train type goes through a specific methodology for recovering the absorbing solution or adsorbent media. After recovery of the train is completed the samples are sealed, uniquely labeled, and shipped under strict Chain-of-Custody to the laboratory for analyses. The collection data from the Batch Trains are recorded on field datasheets and entered into MS Excel spreadsheets to calculate the precise collection volume. This volume is used in conjunction with the specific compound mass determined by the laboratory to calculate a resultant gas stream concentration.

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